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LIQUEFIED NATURAL GAS SAFETY RESEARCH OVERVIEW

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By
Dr. Alan L. Schneider

Prepared for

U.S. DEPARTMENT OF TRANSPORTATION
United States Coast Guard
Office of Merchant Marine Safety
Washington, D.C. 20590

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16. Abstract

Liquefied Natural Gas (LNG) is a growing factor in the United States' energy supply situation, both for periods of high demand (peak shaving) and for daily supply (base load). Safety has been a major issue in its acceptance by the public, the government, and industry. Perhaps because of this, industry and government have undertaken programs of research, development, testing, and evaluation that are more extensive than those for most other new hazardous materials. This paper records the experimental and theoretical work performed with the goal of increasing LNG safety, and has been organized in fourteen divisions: land storage tank studies, rollover, dispersion from spills on land, land spill fire studies, land spill fire protection, ship studies, flameless explosion, dispersion from spills on water, underwater releases, water spill fire studies, vapor cloud deflagration, vapor cloud detonation, physical properties, and gelation. Examining the record of the LNG research effort leads inevitably to the conclusion that there is a basic understanding of the material, sufficient to design, operate, and regulate LNG transportation and storage.

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Presented at the 1978 American Gas Association-Cryogenic Society of America LNG Terminal & Safety Symposium, San Diego, California, 12-13 October 1978

The opinions or assertions contained herein are the private ones of the writer and are not to be construed as official or reflecting the views of the Commandant or the Coast Guard at large.

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The report, "Liquefied Natural Gas Safety Research Overview," was prepared by Dr. Alan L. Schneider of the Cargo and Hazardous Materials Division for presentation at the LNG Terminal & Safety Symposium, San Diego, California, on 12-13 October 1978. The symposium was jointly sponsored by the American Gas Association and the Cryogenic Society of America.

This report reviews and critically analyzes the safety research performed with the cryogenic fuel Liquefied Natural Gas (LNG), now being imported into the United States in increasing quantity. Questions relating to safety are of paramount importance in designing, operating, and regulating the transportation and storage of LNG. There has been a significant amount of safety research completed to date, and this paper describes those projects in the open literature and assesses the future research needed to insure the safety of the LNG industry. While the opinions expressed are solely those of the author, the major portion of the report is a straightforward presentation of the facts.

The report will be of help to many in the LNG field, including those charged with LNG safety, and it should serve to delineate all that has been done to increase the safety of the LNG industry. Since the report will be useful to those outside the Coast Guard as well as to those within, the report has been reprinted to facilitate its circulation nationwide. Comments and recommendations are solicited and should be sent to the Chief, Cargo and Hazardous Materials Division (G-MHM/83), U. S. Coast Guard, Washington, D.C. 20590.

Henry H. Bell

HENRY H. BELL
Rear Admiral, U. S. Coast Guard
Chief, Office of Merchant Marine Safety

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I. INTRODUCTION

Liquefied Natural Gas (LNG) is a growing factor in the United States' energy supply situation, both for periods of high demand (peak shaving) and for daily supply (base load). Safety has been a major issue in its acceptance by the public, the government, and industry. Perhaps because of this, industry and government have undertaken programs of research, development, testing, and evaluation that are more extensive than those for most other new hazardous materials. Maximum safety is possible only through adequate testing. It is likely that had such a program been pursued prior to the design and construction of the installation in Cleveland, Ohio, the 1944 tragedy would have been less severe or would not have occurred at all.

This paper attempts to record the experimental and theoretical work performed with the goal of increasing LNG safety. This paper does not, however, attempt to describe the requirements for LNG transportation and storage. Research of a purely numerical nature such as risk analysis or of a purely commercial nature such as ship voyage scheduling are not included. This is not to suggest that there is a lack of validity or of value in such research, only that the emphasis in this paper is on safety research. Although every attempt has been made to be comprehensive, undoubtedly several valuable studies have been unintentionally left out, despite the fact that they have been published in the open literature. Other projects have not been published, but contain useful information. Anyone having information of any study not included here but that could have been, please contact the writer. Similarly, although every attempt has been made to be accurate, should any questions arise, please bring these to the attention of the author.

The major criteria for including a safety study are that the project has been described in the open literature and has been completed; there are exceptions to this. The LNG safety research studies have been divided into fourteen categories. Where overlapping occurs, some projects are described in two or more categories. The length of each section reflects not the intrinsic importance or merit of the problems studied in each section but rather the volume of projects attempting to solve those problems. These research projects fall into three sections, those dealing with shore-side facilities, those with water transportation, and those independent of land and water.

All opinions are those of the writer and not of the U. S. Coast Guard or of the Federal Government. Government and industry have performed a considerable amount of work with

LNG and will continue to do so. Examining the record of the LNG research effort leads inevitably to the conclusion that there is a basic understanding of the material, sufficient to design, operate, and regulate LNG transportation and storage. Future research will "fine tune" this understanding, perhaps allowing the use of less conservative values in design and operation. Also, new materials of construction and techniques of operation will have to be as rigorously tested as the old ones were. For future research, a more cost-effective procedure would be to invest available research funds in those hazardous chemicals whose behavior is not as well understood as LNG.

II. SHORE-SIDE RESEARCH

A. Land Storage Tank Studies

The LNG land storage tank is very important from the point of view of safety. The only fatal accidental release of LNG in the United States was probably due to faulty tank materials of construction in Cleveland, Ohio, in 1944. Also, the Staten Island tragedy occurred while workmen were inside a storage tank of novel design, repairing it. Safety studies of LNG tanks cover more than design, however, as operations such as purging can have a major impact on the safety of LNG tanks. Note that much of the materials of construction work has applicability to ships' tanks as well.

The factor usually cited as being responsible for the 1944 disaster in Cleveland, Ohio, was that the tank metal underwent brittle fracture due to an insufficient quantity of nickel in the steel alloy; other design factors contributed to the tragedy after the cryogen release. Nine percent nickel steel has been shown suitable for use with LNG, and there has been a large body of work done in this area. One of the more important studies was performed by Zick et al, in which full-scale tanks were tested to destruction at -196°C. The goal of the test series was to prove the suitability of nine percent nickel steel in the quenched and tempered condition and to show that stress relieving was not necessary for steels heat treated by quenching and tempering or by double normalizing and tempering. Nine tanks were built, three rectangular, 2.44 m by 2.44 m by 1.98 m, and six cylindrical, 1.22 m in diameter and 3.96 m long. The rectangular tanks were subjected both to impact as well as to internal pressure while the cylindrical tanks were tested only under internal pressure. The rectangular tanks proved ductile even at -196°C. The quenched and tempered material proved superior, and the burst strengths recorded were from four to six times the ASME code design stress. The ASME later approved nine percent nickel steel of either heat treatment (Zick et al, 1962).

Spaeder and Berger examined the factors that make nine percent nickel steel strong and tough. The steel was quenched and tempered in this instance, and tempering time and temperature was shown as being extremely important in determining properties. Samples of plate 15.2 cm by 20.3 cm by 1.27 cm were tempered for 0.5 hr to 100 days at temperature ranging from 500°C to 700°C. The metal was examined under a light microscope, and underwent tension, impact, and microhardness tests. Plots were prepared relating the strength at various temperatures and impact energy properties as a function of time at various temperatures. They concluded that tempering significantly affected the volume fraction of the various metal phases (Spaeder and Berger, 1970).

Benter and Murphy of the U.S. Steel Corporation, as a part of a program entitled "Operation Cryogenics," studied the toughness of nine percent nickel steel. Their effort focused on the fracture characteristics of quenched and tempered steel at -196°C using the drop weight test and the crack starter explosion-bulge test. Four plates 1.27 cm or 1.90 cm thick were tested. Charpy V-notch impact tests were run at -196°C, -229°C, -253°C, and -263°C. Drop weight tests were performed at -229°C, -253°C, and -263°C by the Battelle Memorial Institute. The Nil Ductility Transition (NDT) temperature for the thin plate was below -263°C. Explosion-bulge tests also showed that the NDT temperature was below -196°C. The test series proved that nine percent nickel steel remained ductile at temperatures much lower than LNG temperatures (Benter and Murphy, 1967).

Maruoka, of the Sumitomo Metal Industries, Ltd., reported on the development of a submerged-arc welding technique for nine percent nickel steel large diameter pipes for LNG. Two problems had to be overcome, the occurrence of weld cracks, and substandard weld joint properties. An extensive experimental program showed, for example, that molybdenum was effective in decreasing cracks. He found that Hastelloy C wire, which contained both molybdenum and tungsten, and a ZnO_2-SiO_2 base flux produced satisfactory weld properties even at -196°C. Coefficients of thermal expansion of the welded metals were almost equal to the virgin metal. Pilot production of welded nine percent nickel steel pipes was successfully accomplished (Marouka, 1975).

The International Nickel Company, Inc. published a compendium of research on the low temperature behavior of nine percent nickel steel over a wide range of temperatures, but with emphasis at low temperatures. Some of the topics covered include chemical composition, heat treatment, impact properties, fracture toughness, hardness, fatigue, and weldability. A short description of some of the experimental details for most topics was included (International Nickel Company, 1975). This collection of data is useful in that it demonstrates the suitability of nine percent nickel steel for LNG service. References are given for the primary papers.

Cordea et al, from Armco Steel, investigated the properties of five percent nickel steel. Cost was a major consideration with five percent nickel steel being about 20% cheaper than the nine percent nickel steel alloy. Yet with a three step heat treatment, their CRYONIC 5 alloy had toughness equivalent to nine percent alloys. Cordea reported measured properties of the five percent alloy, comparing the properties with those from stainless steel, and nine percent nickel steel. Some of these properties were the Charpy V-notch toughness, yield strength, modulus of elasticity, and thermal expansion coefficient.

The data indicated that the five percent alloy was acceptable for LNG service (Cordea et al, 1972). Despite this, there has not been a wide acceptance of five percent nickel steel in this country.

The Aluminum Company of America has prepared a compendium of aluminum properties for cryogenic service. Aluminum, the major competitor of nine percent nickel steel for LNG service, was used extensively in the space program and is widely used in land and ship LNG tanks. Data were given for low temperature toughness and tensile strength. Tensile strength actually increased as the temperature decreased, both for virgin metal and, to a lesser extent, welded metal for at least one aluminum alloy and weld filler alloy. Also discussed are impact tests, tear resistance, fracture toughness, and fatigue strength. References were given for the data, plus occasional experimental details (Aluminum Company of America, 1974). The results show that aluminum is a suitable material of construction for LNG service.

Concrete, too, is a suitable material for LNG service. Wozniak, of Chicago Bridge and Iron (CB&I), and Salmon and Huang of Sergent and Lundy, studied the feasibility of concrete as a secondary containment barrier. There had been interest in tall concrete dikes close to the tank in addition to low earthen dikes further away from the tank. A pre-stressed concrete wall, reduced in scale, was designed and built for a series of cryogenic tests. A computer analysis was performed to aid in the design stage; pre-stressing was identified as necessary to avoid vertical crack propagation. In case of tank failure, the wall may suddenly be thermally stressed to LNG temperatures, exposed to thermal radiation if the LNG is ignited, and subjected to the full liquid head. Vertical and horizontal cracks were cast into the wall to serve as crack starters. A large number of defects were observed after the casting forms were removed; these were repaired, but they did serve as additional test structures. Two tests were run with the test wall, one test with full pre-stressing and one with only partial pre-stressing. Some LNG leakage did occur, but this was small and related to the wall defects. The test wall, they said, performed generally as predicted in the design stage (Wozniak et al, 1975).

Hashemi and Wesson of University Engineers examined pressure control systems to minimize tank pressure variations so as to reduce boiloff losses. As normal boiloff occurs, due to heat leakage through the insulation, the pressure in the vapor space increases as well until venting occurs or a boiloff compressor is activated. Sudden changes in atmospheric pressure can cause rapid vaporization as well. Unless there is a proper understanding of these vapor generation rates, pressure control systems can be over-sized leading to

inefficient design. They developed two boiloff rate equations, the first for evaporation which is controlled by the variation in saturation temperature with pressure and by the temperature difference between the LNG surface and bulk temperature. The second equation accounted for the vapor produced when the atmospheric pressure drops. With their model the tank designer can avoid an oversized boiloff compressor that could produce a partial vacuum in the storage tank, generating still more vapor (Hashemi and Wesson, 1971).

How the components of LNG individually vaporize is important, for the problems of rollover and Flameless Explosion depend on the concentrations in the tank. It can also be important in terms of designing send out systems and in custody transfer. Aging, or weathering of LNG was investigated by Shell Pipeline Company (Engar and Hartman, 1972), as discussed in the Flameless Explosion phenomenon section of this paper. Shah and Aarts of CB&I investigated aging by preparing a mathematical model that calculated the heat leak rate into land storage tanks and the component vaporization rate for each time interval. The initial tank conditions had to be known to use the model. The model required thermophysical properties of LNG mixtures that were developed by others and sample calculations were provided (Shah and Aarts, 1973). The sample calculations presented demonstrate convincingly that there is significant compositional change due to weathering.

Tank operation is relatively straightforward; the difficulties come about when a tank is taken into or out of service, since if done incorrectly, a flammable mixture could result inside the tank, leading to disaster. Hanke et al, of CB&I, reported in 1974 on several related research projects. Perlite, an expanded inorganic insulator, when mixed with methane and air, burned at the perlite surface but would not burn below the surface; the glass fiber resilient blanket burned weakly, with the binder material being eventually consumed. About 3-5 m^3 of methane at standard conditions was absorbed on each m^3 of perlite. Nitrogen was successfully used as a purge gas for methane in perlite with and without a resilient blanket. Hanke also developed a mathematical model for the quantity of purge gas required. Four absorption-desorption tests indicated that the amount of methane absorbed equaled that desorbed; the resilient blanket had the effect of lengthening the desorption time. Tests of the flammability of insulation materials demonstrated that the few flammable materials used in tanks did not present a significant threat. The authors then described their tank design and the provisions made for purging. A comparison of their purging models with the actual field data showed reasonable agreement. They concluded that the purging of LNG tanks into and out of service safely was feasible (Hanke et al, 1974).

The LNG storage tank is a most important element in the LNG system. Since 1944, a great deal of research has been performed on materials of construction and on the tank design and operation. As new insulations and novel construction materials are proposed they should be tested as thoroughly as nine percent nickel steel and aluminum have been.

B. Rollover

One of the unexpected occurrences in the Liquefied Natural Gas industry occurred on August 21, 1971, at the SNAM terminal at La Spezia, Italy. About 18 hours after the completion of cargo transfer from the LNG carrier ESSO BREGA, the tank pressure suddenly rose and the safety valves opened; about 318 m^3 of LNG vaporized and was released. Fortunately, there were no injuries nor was any damage done (Sarsten, 1972). This incident, and several others like it have prompted extensive research. Since few are willing to risk overpressurizing LNG tanks, research has concentrated on computer simulations and small-scale experiments with non-cryogenic analogs.

The conventional explanation of this rapid vaporization is embodied in its name, rollover. If the composition of the tank contents and of the LNG being added are different, stratification will result if mixing does not occur on loading. The different compositions can arise either from different sources of the liquid or from aging of the tank's contents. The higher density, methane poor layers on the bottom are warmer, and the vaporization is suppressed by the lower density, cooler, methane rich layers on top. Mixing between layers is slow and only the top layer is in thermal equilibrium with the vapor space. As lower layers warm, the density differences decline until the densities are about equal; then the layers rapidly mix, hence the term rollover. Similar phenomena can be studied in salt solutions. Now as the warmer layer or layers reach the topmost layer, the suppressed vaporization is released and rapid flashing occurs. The danger lies in overpressurizing the tank or of a large vapor cloud issuing from the safety valves (Smith et al, 1973). Periodic or continuous pumping of a denser layer to the top of the tank is not a complete solution, however.

Air Products and Chemicals, a manufacturer of components of LNG liquefaction plants, has studied this problem. Geist and Chattergee developed a computer simulation for use in establishing guidelines for reducing the chances of layering. They modeled a multi-layer system by creating heat and mass balances. Heat and mass flux rates measured in salt water layered systems were adapted to LNG systems. This model well simulated the historical record in three very different rollover incidences and led to recommendations on ways of avoiding rollover, including the now standard top loading of LNG that is heavier than the tank heel and bottom loading of LNG that is lighter than the heel (Geist and Chattergee, 1972). While single component substances can not spontaneously stratify, it is possible for some LNG compositions to do so. Since nitrogen is often present in small proportions and its

density is greater than methane but its boiling point is lower, auto-stratification is possible followed by rollover. As energy leaks into the well-mixed liquid, nitrogen preferentially boils leaving a surface layer cooler than the bulk but with a lower density, leading to stratification. There has been at least one incident of this type. While Chattergee feels this can not occur when the nitrogen concentration is below 0.5%, it can occur when the concentration is above 4%, with the behavior between 0.5% and 4% being uncertain. Prevention by eliminating nitrogen is the only solution, as recirculation will only add energy to the system, making the top layer even cooler (Chattergee and Geist, 1976).

Cabot Corporation, owner of the Distrigas LNG receiving terminal at Everett, Massachusetts, also studied rollover. Since aging can occur in the tank heel due to the long time between deliveries, concentration differences could be significant between the ship's cargo and the shore facility's tank content. The Cabot model uses a multi-layer system with two components, methane, and a single pseudo fluid representing all other liquids. The model is significantly different from the Air Products and Chemicals model, but, as with the Geist model, diffusivities are developed by analogy with salt solutions. The model shows good agreement with the La Spezia incident (Germeles, 1975).

There have not been any reported cases of rollover aboard LNG carriers. This is probably due to the fact that before loading at an export terminal the vessels tanks are virtually empty. Too, the vessel's voyage is relatively short and mixing is aided by the ship's motions in a seaway.

The limitations of these models lie in the poorly understood physical and transport properties of light hydrocarbon mixtures near their mixture boiling point and the near impossibility of experimental verification of results. Furthermore, the number of rollover incidents with detailed descriptions in the open literature is very limited. Nevertheless, the phenomena is well understood and the rollover models can give at least some warning of the possibility of rollover that may occur in loading land storage tanks.

C. Dispersion From Spills On Land

One of the lessons learned from the Cleveland, Ohio, disaster in 1944, and from storage tanks in general, is that sufficient diking for catastrophic tank failure is necessary. Furthermore, a desirable design feature for LNG storage facilities, and one that might become required at the national level, is that a flammable vapor cloud not cross the facilities' boundary line. This provides the motivation for studying boiling rates on land and cloud travel over land.

Curiously, spills on land are approximately the opposite of spills on water. The area of the land spills is determined by the dike walls while the area of the water spill continuously expands. Also, the ground soon freezes, leading to a low steady state vaporization rate, whereas water does not seem to freeze under a water spill. Together this means that on land there is a peak vapor generation rate towards the beginning of the spill, dropping off to a much lower steady state rate. With water spills, the vapor generation rate increases throughout the spill as long as the pool expands, because the energy rate of input from the underlaying water remains constant. Another difference is that the water spill is always modeled as unconfined and on a flat surface, but land spills always have dikes that present obstacles to the vapor dispersion. Unlike the smooth surface of water, the dike floor can be rough or smooth, and can be composed of different materials. These distinctions between the two types of spills require separate evaluations.

In 1960 and 1961, Conch conducted a pioneering series of small scale spill tests on land at Lake Charles, Louisiana, in preparation for large volume international trade in LNG. A 1.52 m X 1.52 m diked area was used with sensors placed along the downwind axis at the dyke wall and 3 m from the dike. The sensors were placed at heights up to 0.69 m above ground level. The peak vaporization rate lasted only for a short period, leveling off to a low steady state value, with the flammable downwind zone following the same pattern of being flammable for longer distances initially, reducing to shorter distances as the dike floor froze. At steady state the vapor concentration was distributed normally as a function of height. (Conch, 1962, Arthur D. Little, 1971). This work is not as refined as more current work, but, in the context of its day, it was useful. It established several principles about land spills but over-estimated the buoyancy effects of the cold LNG vapor.

Gaz de France was one of the first companies to construct LNG terminals. In preparation for one terminal they conducted a series of tests at Nantes with a series of four

diked areas, 3 m X 3 m, 6 m X 7 m, 7 m X 7 m, and 14 m X 14 m. They also measured the vaporization rate of LNG on various types of soils in order to account for the initial flash from a land spill. A Gaussian model was modified for use in correcting the data from the spill tests. Deviations from the time average vapor concentration appeared significant when the average concentration fell below 3%. They concluded that only massive spills could lead to significant vapor travel as the largest diked area, about 200 m^2, gave rise to a flammable vapor cloud travel of only 100 m, this being the initial flash (Humbert-Basset and Montet, 1972, Gideon et al, 1974-II).

One of the largest LNG research and development efforts was carried out for the American Gas Association (AGA) during the late 1960's and early 1970's. One major part was the early TRW spill series. In this test series a 1.5 m diameter diked area with 0.15 m high walls was used in 0.19 m^3 spills. Boiloff rates were varied by changing the water content of the clay soil dike floor. The vapor concentrations were measured using sensors located 15 m and 30 m downwind from the dikes. Measurements were taken in the vertical and in the crosswind direction at the two stations (Arthur D. Little, Inc., 1971). The test results have been superseded by later tests but are important for historical reasons. These tests were analyzed by Wilcox.

Wilcox prepared an empirical dispersion law for the AGA. He used the TRW data just described. First, he "guessed" the functional dependence of concentration with the distances downwind, crosswind, and vertical; the dike diameter; and the wind velocity. Then the various constants were derived using the experimental data. The final results differed from the more common dispersion equations. Wilcox's form is Gaussian, but the exponents are not of the usual form. For example, the velocity of the wind usually appears as inversely proportional to vapor concentration; Wilcox correlates it as inversely proportional to the square of concentration. Also, the weather cannot be factored into the equation. (Wilcox, 1971). Deviation from the current types of equations is probably due to the very limited amount of data available from the TRW tests and, perhaps, to the small spill sizes.

The next effort was a large series of spills carried out by Battelle Columbus Laboratories (BCL) at the TRW Capistrano Test Site (CTS) in California for the AGA. Dispersion tests were run from diked areas 1.8 m, 6.1 m, and 24 m in diameter. Spill sizes were 0.38 m^3, 4.6 m^3, and 51.3 m^3 of LNG, respectively. The LNG was 0.10 to 0.15 m deep and assayed 71% to 96.6% methane, with most tests performed with at least 90% methane concentration. A three dimensional array of up to 36 MSA sensors were used in these tests, with a thermocouple at each sensor. Also, thermocouples were placed in the bottom of the

dike. The LNG level was measured and the local weather conditions were monitored. Some 28 land spill dispersion tests were run and the data analyzed for each. BCL noted significant cracking in the dike floor; this cracking was associated with short term increases in the vaporization rate. These increases were superimposed on the usual initial peak vaporization rate followed by a dropoff to steady state (Duffy et al, 1974).

Arthur D. Little, Inc. (ADL), as part of this AGA project, developed a model for vapor dispersion from a diked area based on the TRW data and other work. The multiphase model began with an analysis of the time required to fill the dike volume with vapor, the cryogen spill time being assumed essentially zero. The second step calculated the flow rate of the vapor over the lee edge of the dike by calculating the total mass flow rate followed by a positioning of the vapor on the dike edge. The dispersion is Gaussian using a line source as the dike edge. The model agreed well with the experiments except within one dike diameter from the dike. Some small modifications were made to the classical Gaussian expression to account for complicating factors. Further work was recommended with weather conditions more stable than the unstable to neutral that TRW found at the CTS. A computer program was prepared for the model (Drake et al, 1974).

Welker of University Engineers analyzed the CTS tests. The boiloff rate on land was developed for short times considering only the energy input from the soil, while for long times convection from air, radiation from the sun, and sensible heat from the LNG itself played a role. Using a classical Gaussian plume model and the data from the 24 m test from the TRW series, he compared the experimentally measured concentration data with his calculated concentrations using Brookhaven weather condition "C", neutral. These comparisons were performed for each of the 36 sensor locations used in the test. Generally there was good agreement between them, with reasonable scatter from the sensors. There was some difficulty in situations where the calculated concentration was less than 0.01% - there were peaks of short duration close to or exceeding 5% (Welker, 1974-II). The model works well in predicting average concentrations but does not allow for pockets of gas that may be flammable.

For the AGA Parker compared his 1970 model to the data correlated by BCL from the tests at the CTS. Parker's model had its basis in the classic Gaussian plume model with modifications for vapor negative buoyancy and for the presence of the dike wall. This model showed general agreement with the data from the 0.45 m high dike walls used by BCL in their tests. His calculations predicted that increasing the dike height from 0.45 m to 2.4 m

would reduce the distance the flammable vapor cloud would travel by a factor of 2. Similarly, increasing the height from 0.45 m to 4.9 m would reduce the downwind travel distance by a factor of 3 (Parker, 1974).

The American Gas Association effort was a very productive one and the results are useful today. Until the expected Department of Energy spill tests are run, the CTS series will remain the most comprehensive. Also of use are the several land dispersion models developed and compared to the experimental results. In particular, the initial flash problem is addressed. Weaknesses in the experimental program include the lack of stable weather tests.

The BCL tests at the CTS were limited in that they were not conducted in stable weather conditions but only in unstable and in neutral conditions. This was a serious limitation, for the existence of an inversion could make a significant difference in the downwind hazard. BCL performed two additional tests at the West Jefferson test facility for the AGA. These tests were run in a 1.8 m diameter dike with a low dike wall to measure dispersion during an inversion. They had three other objectives, better LNG depth instrumentation, an improved dike floor, and a major emphasis on safety; otherwise the tests were similar to those at the CTS. The dike floor at the CTS had cracked and this increased the effective area while the new dike floor was uniform and resistant to cracking. The gas sensors used were the same as those at the CTS, but, unfortunately, at the time the new tests were run, the sensors had either failed or did not perform accurately. The results of the tests showed that the sensors were not performing properly, hence, there were no acceptable quantitative concentration data. The improved dike floor, mylar over brick, caused the low evaporation rate steady state to be reached much more rapidly than the CTS soil floor. BCL personnel felt they had demonstrated the feasibility of tests performed under inversion conditions. (Gideon et al, 1974-I). Their idea was correct - if at all possible, stable weather conditions should be used in dispersion tests along with neutral and unstable conditions. The dike floor work suggests that it may be possible to reduce the hazards from the initial flash by designing the dike floor with that goal in mind. Since the steady state vaporization is likely to be less of a problem than the initial flash, the latter is generally the more hazardous.

The Japan Gas Association was commissioned by the Natural Resources and Energy Agency of the Japanese Government to conduct a series of LNG vapor dispersion and fire

tests. These were conducted at the Sodegaura terminal of the Tokyo Gas Company, Ltd. The 1974 tests involved two 2 m by 2 m diked areas and the 1975 test a 10 m by 10 m diked area, plus ignition tests. These tests were well instrumented; for the dispersion tests, 72 gas sensors were employed. Spill tests were run (three in the 10 m by 10 m dike), one on water in a diked area (to simulate water spills), and two burns on land. A classical Gaussian dispersion model was used to correlate the dispersion data, but, with neutral weather conditions, the dispersion coefficients did not reflect the strong layering found by many others (for example, Burgess et al, 1970, 1972). Also, concentration profiles were developed (Japan Gas Association, 1976). The results are somewhat different from those of other experimenters.

Meroney, of Colorado State University, has been involved with wind tunnel simulations of LNG spills with the support of the U.S. Department of Energy (DOE). A test of this technique involved the simulation of one of the American Gas Association (AGA) land spills at the Capistrano Test Site. The entire spill sequence was simulated; carbon dioxide or cooled helium-nitrogen mixtures were used to simulate LNG densities. While many of the test parameters could be scaled down for the wind tunnel, not all could be scaled down at the same time. A wind tunnel test section 1.8 m by 1.8 m by 29 m long was used, with temperature-controlled air stream and boundary walls. Test results included a qualitative, visual study of the flow field around the dike and tank structures and a quantitative measurement of gas concentrations produced by a tracer released from the diked area. Meroney found good agreement with the AGA test. Future plans include pretest simulation of each test planned in the DOE LNG spill test program, to help in such matters as instrument placement (Meroney et al, 1978). While this technique cannot substitute fully for field tests, it can aid in planning. Due to the extremely high costs involved in large spill tests, any preliminary work performed in wind tunnels can be beneficial. Further experience with wind tunnels will demonstrate exactly how useful they can be.

Spills of LNG on both land and water have been run. These tests are few in number; large LNG spills are difficult to perform and are fairly expensive to run. If the results from land spills could be used for water spills, and vice versa, a significant increase in the spill data base would be made. Gideon of BCL critically examined most of the spill tests to that time for the AGA. He found different correlations for concentrations close to the spill and far from the spill; also, instantaneous spills led to different correlations from those for continuous spills. For water spills, the variables used were X (distance), C (concentration), M (mass spilled), $\dot{M}$ (Mass spill rate), and U (wind velocity). For land spills, A (area) was

substituted for the mass variables. For short distances the correlations used were $XC/M^{3/4}$, and XC/A, while for long distances, the correlations were $X^2C/\dot{M}$, $X^2C/M^{3/4}$ and X^2C/A. The experimental data correlated equally well with or without the wind velocity, so another set of correlations were prepared, the above correlations being multiplied by the velocity "U." Gideon concluded that instantaneous spill data could not be used with continuous spills. Differences between instantaneous land and water spills could be accounted for by varying the vaporization rate. Water spills were, it was concluded, difficult to instrument, especially in determining the pool area on water as a function of time. Correlations between instantaneous spills on land and on water differed by a factor of seven. (Gideon et al, 1974-II). This effort was a well intentioned one, for the goal of being able to interchange land and water spill experimental data is excellent. The results, however, do not demonstrate complete success. The first and second power exponents on the distance term are surprising, since in the Gaussian model the exponent is a function of weather and not the first or second power but typically somewhere in between. More effort is required in this area before the data can be confidently interchanged between land and water spills.

The record of spills of LNG on land is extensive and will grow if the proposed Department of Energy experiments are executed. Further work during thermal inversions would be helpful. Also, more work is needed on developing dike floor and wall materials that will reduce the duration and amount of the initial vapor flash. The effect on the boiling rates of LNG in tall dikes needs more work including the volume increase due to vapor bubbles rising in the cryogen, which could cause LNG to overflow the dike wall. Finally, a better understanding of the peak-to-average concentration ratio in the vapor cloud is needed.

D. Land Spill Fire Studies

The major hazard from land storage of LNG is a release of cryogen followed by ignition. Vapor cloud deflagration and detonation are discussed in their respective sections; unconfined detonations are unlikely, and a vapor cloud arising from a land spill, once ignited, is likely to burn back to the source, a diked pool of LNG. The land pool fire is therefore the major hazard. Since the peak vapor generation rate occurs when the LNG first contacts the unfrozen dike floor, the fire resulting is then larger than when the ground is frozen and the vaporization rate has fallen to a lower steady state rate. Various governmental and industrial safety codes specify the maximum thermal energy flux at the plant boundary line based on the relationship of a given flux for a specified time leading to a certain level of injury; this is usually given as 3.2 kW/m^2 to 32 kW/m^2. The wide discrepancy is based on differing judgment on the acceptable level of damage to innocent bystanders; the most reasonable figure probably lies somewhere between these values. Predicting the thermal flux at a distance from a given fire is a significant problem for the LNG industry and much has been experimentally done in this area to determine radiation fluxes and to model fires.

Conch performed a series of large fire tests at Lake Charles, Louisiana, as part of the 1960 and 1961 research effort at the U.S. Bureau of Mines. Dikes of 1.5 m by 1.5 m and 6.1 m by 6.1 m were used in these tests. For comparison, gasoline was burned - the flames from gasoline and LNG were similar in size; the gasoline flame was very sooty while the LNG flame was clean. They found the average radiation for LNG was 750 kW/m^2 and for gasoline it was 540kW/m^2. They pointed out that the 50% higher heat of combustion for gasoline approximately compensated for LNG's higher boiling rate, and made the following three qualitative observations: flame heights were roughly three times the diameter, wind reduced the flame height, and no frothing or boilover occurred (Conch, 1962, Burgess and Zabetakis, 1962).

Burgess and Zabetakis of the U.S. Bureau of Mines, with partial support from the Continental Oil Company, conducted an experimental program of LNG spills and burns; this work and the Lake Charles tests discussed above were a part of the same test effort. The percentage of thermal energy radiated was as much as 34%, suggesting that all hydrocarbons burning in large diameter pools will radiate about the same fraction, perhaps as high as 38%. Burning rates of shallow LNG pools proved quite difficult to measure accurately, but values as high as 1.16 cm/min were measured. On a volume basis LNG burned faster than gasoline.

The thermal radiation per unit area of fuel was between 750 kW/m^2 and 860 kW/m^2 for LNG in 3.0 m diameter pools and it declined as the pool diameter increased. Similar values for gasoline were observed for smaller pool diameters, then the radiation flux declined for larger pools. Ignition of vapors above LNG pools within the peak vaporization rate period produced a large momentary flash but no overpressure or liquid splashing. The ignition of LNG in the steady-state vapor-ignition period lead to a steady state flame. They concluded that LNG can be safely stored in above ground diked tanks (Burgess and Zabetakis, 1962).

The American Gas Association (AGA) work on dispersion included fire tests. The goal was to run experimental pool fires and to develop predictive models. Duffy of the Battelle Columbus Laboratories (BCL), ran the dispersion and fire tests. Fire tests were run at the TRW Capistrano Test Site (CTS). Radiation measurements were obtained using wide and narrow angle radiometers, total heat flux meters, wood samples, skin simulants, grating spectrometers, and pyrometers. Thermocouples were placed with the wood samples, placed downwind to measure air temperatures, and placed above the dike floor to measure vapor temperatures. There were fourteen fire tests: seven 1.8 m diameter fires, six 6.1 m diameter fires, and one 24 m diameter fire. The largest test was not complete as some equipment failed before the fire covered the entire surface. The highest vaporization rate was 1.6 cm/min, and the highest radiation flux (average values for the same test) was about 62 kW/m^2, which was recorded from the 24 m diameter test. They developed a general method to calculate the radiation flux to a target surface based on the test results. The method considered the source intensity; flame base size; vaporization rate; flame shape (including "holes" in the flame, flame height, and flame tilt angle); and the geometric view factor. They concluded that the source intensity was about 178 kW/m^2 (Duffy et al, 1974). The value of the source intensity seems rather high relative to other hydrocarbons but not impossibly so; the methodology used for calculating the incident radiation on a target is useful.

Welker, of University Engineers (UE), analyzed the data from the BCL tests. He included some data from tests at the Ansul test facility at Marinette, Wisconsin. The radiant fluxes from the radiometers, skin simulants, and wood blocks lead to an estimate that an optically thick flame would have a flux of about 143 kW/m^2. He provided a simplified method for calculating radiation fluxes using the view factor, fire base size, and the flame tilt angle. He also developed a more complex, more exact model approach as well (Welker, 1974-I).

Attalah and Raj of Arthur D. Little (ADL), as part of the analysis of the BCL tests, were charged with selecting and, if necessary, modifying a model that would correlate the

experimental data. After considering the existing LNG burn experiments, they estimated the total emissive power of the flame to be 100 kW/m^2. The model selected was similar to Welker's but some of the terms differed in value. A computer model was prepared for determining the radiant flux; this was a comprehensive, all inclusive model, including such factors as the "wet soil thermal conductivity." A listing of the computer program was included in the report (Attalah and Raj, 1974). Rationalizing the emissive power values of 178 kW/m^2, 143 kW/m^2, and 100 kW/m^2 is very difficult. Since this is such an important parameter in all thermal radiation models, better agreement is desirable.

Carpenter and Shackleford of TRW examined the spectral data from the BCL tests and the CTS. Several infrared spectra were reproduced and analyzed. They concluded that, for LNG's with higher hydrocarbons present, the greatest thermal flux occurs towards the end of the fire when the higher hydrocarbons are present in greater concentrations. The carbon soot emission then predominates as well. At least for the 1.8 m diameter fire, the lower the wind speed the higher the thermal radiation. Also for the 1.8 m fire, there were intensity fluctuations (with an instrument time constant of 0.3 seconds) of a factor of over 100 for narrow field measurements and of about three for wide field measurements, with flame temperatures as high as 1400^{o}K (Carpenter and Shackleford, 1974).

The comprehensive AGA work has provided good data for land fires. Until the U.S. Department of Energy studies are complete, the AGA tests must be considered the definitive test series.

May and McQueen of ESSO Research & Engineering Company had the opportunity to measure the thermal radiation from a very large, irregularly shaped LNG fire. While the LNG input rate to the burning trench was well defined, 2150 m^3/day to 6360 m^3/day, the pool area was poorly defined. Radiometers were located at various distances along three directions, at ground levels and at elevated locations. They used a point source model for the land fire, similar to Burgess' model for an LNG spill fire on water (see Burgess et al, 1972). A very important parameter for such models was how much of the combustion energy is radiated outward. Time-averaged values of the radiated energy as a fraction of the total energy showed that only about 16.4% of the energy was radiated. This value was measured using elevated radiometers; a lower value of 12.4% was measured using ground level radiometers, because the dikes tended to shield some of the fire from the radiometers at ground level (May and McQueen, 1973). Note that Burgess reported a much higher fraction of the total energy radiated, 34%, from the Lake Charles tests.

The Japan Gas Association carried out a series of spill tests involving dispersion and fire at the Sodegaura terminal of the Tokyo Gas Company Ltd. in 1974-75. These safety tests were commissioned by the Natural Resources and Energy Agency of the Japanese Government. Combustion tests were performed in 2m by 2m square dikes with LNG being continuously added. Three combustion tests were run; unlike the previous tests elsewhere, the LNG was more than 99% methane, coming from Kenia, Alaska. Ignition was difficult; unless the igniter was placed some distance into the visible cloud, ignition would not occur. Only about 13% of the total energy was radiated outward, and the total radiant flux from the flame surface was about 58 kW/m^2, low probably due to the sootless methane flame. (Japan Gas Association, 1976). These values are significantly lower than those found in the AGA tests and demonstrate the effect of LNG composition.

Along with the fire tests there have been several theoretical models developed for burning pools. Wilcox prepared a very theoretical model for a class of fire that included LNG. The model was an involved development with several parts - an entrainment law that described the air input, followed by a thermochemical analysis. He then solved the radiation-heat-loss term, nondimensionalized the equations, and provided the initial conditions. A computer program was written to solve these very involved equations for an LNG fire. Comparison of calculated and experimental flame height data indicated good agreement only for small fires as large fires have "swirl", which was not included in the model (Wilcox, 1975).

Raj of Arthur D. Little presented a state-of-the-art review of LNG fires in 1977. He noted that there were two ways to calculate the thermal radiation flux as a function of distance from a fire. The first way was the simple point source model where complete combustion occurs at the center; the fraction of combustion energy radiated outwards is an important parameter. The receptor radiation flux was determined by dividing the radiated energy by the area of the hemisphere whose radius is the distance from the receptor to the fire center. The second model was the plume flame model, in which the entire visible flame was assumed to radiate energy and the invisible portion was not. The flux to the receptor is the product of the flame's emissive power, the flame's emissivity, the view factor, and the atmospheric transmissivity. Raj evaluated each of these four factors, recommending the best values or calculation methodologies. In particular, he recommended 100 kW/m^2 as the flame's emissive power. Finally, he addressed the two issues of flame height prediction and wind tilting of diffusion flames (Raj, 1977). This is an excellent analysis.

A knowledge of LNG land fires is very important to LNG safety. There are still many questions not completely answered, such as the flame emissive power. Currently, a conservative emissive power level must be used, but further tests may show that a lower level is more appropriate. For safety regulatory purposes, the major problem is determining an acceptable level of thermal radiation. This is a judgmental decision and human life is involved; both facts make this a very difficult problem.

E. Land Spill Fire Protection

Historically, fire protection has been one of the major concerns in LNG storage. Learning how to combat fires has been a major cause of an impressive amount of research. Control of an LNG spill fire is usually the goal, to reduce the rate of burning rather than to completely extinguish the fire, to avoid an unignited LNG vapor cloud drifting downwind and causing even more damage than the original pool fire. Reducing the thermal flux, in some situations, could permit the stoppage of LNG flow. Other actions could be taken to ameliorate the effects of such fires on structures.

Perhaps the first major experimental program was the Conch tests at Lake Charles, Louisiana. Fire extinguishment tests were run in a 6.1 m by 6.1 m diked area. The extinguishing agent was finely powdered sodium bicarbonate dry chemical. Two tests using 91 kg/sec and 25 kg/sec delivered by a turret nozzle extinguished the fire; lower flow rates delivered by hand lines either failed to extinguish the fire or the fuel rapidly reignited. (No extinguishing tests were carried out at the Bureau of Mines facility). Sodium bicarbonate could extinguish LNG fires if about 0.68 kg of powder per second were applied to each square meter of surface; the entire surface had to be covered completely. LNG fires were easier to extinguish than gasoline fires (Burgess and Zabetakis, 1962).

As part of the American Gas Association's (AGA) research effort into LNG hazards, two series of fire tests were held, a 1971 effort at the Philadelphia Gas Works and a 1972 effort at the Ansul fire facility at Marinette, Wisconsin. In both cases several organizations supported these efforts. The goal was to gather data on the effectiveness of high expansion foam and dry chemical agent. Prior to these tests only qualitative information was available on the effectiveness of high expansion foam. Wesson of Wesson and Associates analyzed the test results. Typical foam expansions ranged from 100:1 to 1000:1; they work by diluting the oxygen concentration, preventing free movement of air in a fire, cooling the fire by converting water to steam, and reducing the thermal radiation back to the liquid surface. The spills at Philadelphia were made into 1.5 m and 3.0 m diameter pits while those at the Ansul site were in 6.1 m by 6.1 m dikes and in 9.1 m by 12.2 m dikes. The fire data were taken after precooling, that is, the fires were at steady - state when the data were taken. The Ansul tests were conducted with two types of foam generators and two foam concentrates, one in each generator. Wesson provided data on the fire control time as a function of the foam application rate, of pool size, and of foam expansion ratio, as well as the reduction of thermal radiation as a function of the foam expansion ratio. The latter appeared more effective than using water spray, which was also tested. High expansion

foams significantly reduced the vapor concentration in unignited spill tests. Tests with dry chemicals included potassium bicarbonate, monoammonium phosphate, and urea-potassium bicarbonate. Data were collected on the LNG fire extinguishing time as a function of application rate, pool size and type of chemical. Wesson concluded that certain high expansion foams can control LNG fires, consequently reducing thermal flux. Minimum application rates for dry chemicals were established. The required quantity of foam and dry chemical per unit area of fire were independent of the fire area (Wesson, 1974).

As a continuation of the AGA work, University Engineers (UE) conducted a series of spill tests at Norman, Oklahoma, in which the vaporization rate was varied by using a fire test pan with water pipes installed. High burning rates, up to 3.8 cm/min, simulated the early period in an LNG spill before the impoundment area freezes; 1.5 m and 3.0 m diameter fires were run. The usual methane detectors and radiometers were provided. High expansion foams reduced the vapor concentration by as much as 80% within one pool diameter; the effectiveness of the foam depended on the degree of expansion. The thermal radiation was reduced by as much as 95% by high expansion foams. Finally, the extinguishing time and minimum quantity for extinguishment for dry chemicals was related to the LNG burning rate (University Engineers, 1974). It is clear that the initial contact between LNG and the warm ground required much more effort to either control or extinguish.

The Ansul Company, a producer of fire fighting systems and agents, has been test extinguishing large natural gas fires since 1951 (three series, 246 tests) and LNG pool fires (two series, 143 tests). The LNG fire tests were reported in more detail in Wesson, 1974, and University Engineers, 1974. In a report Ansul provided useful data for commercial extinguishing applications and recommended suitable safety factors. Also, application techniques were briefly discussed (Ansul, undated).

University Engineers (UE) performed a series of small scale fire tests for the U.S. Coast Guard to test several control methods. One major goal was the establishment of a basis for the design of very large fire tests, so large that they would be on the margin of extinguishable LNG fires. UE showed the importance of trained fire fighters in attacking LNG fires, as the minimum chemical application rates and times were not valid for untrained personnel. Obstructions on land and on ship could alter the extinguishment requirements, but UE found that as long as the chemical agent covered the liquid surface, the required agent application rate was not altered. Water spray, to reduce thermal radiation, proved an ineffectual technique. While some beneficial effect was noted, water sprayed directly on the object to be protected would have been much more effective.

Spraying water into LNG vapor clouds showed some benefit, with the water spray facilitating turbulent mixing. Finally, extinguishing LNG fires on water was no different than extinguishing fires on land if correction was made for the greater burning rate on water. All tests were carried out in 9.3 m^2 pool fires (Brown et al, 1976). This test series proved helpful to the Coast Guard's regulatory mission, since it is now responsible for the fire safety of all LNG importation and exportation terminals.

Direct control and/or extinguishment of LNG fires are active methods of protection for nearby structures. For example, a failure of adjacent tanks would compound the hazard from an LNG tank failure, so to the extent possible, tanks should be protected from each other. In some ways passive protection may be superior - insulative coatings are such passive devices. Wesson and Lott of Wesson and Associates, Inc., investigated this issue. They listed the following types of coatings as being acceptable: cement compounds, ablative coatings, subliming compounds, and intumescent mastic compositions. In their opinion the following were unacceptable: standard thermal insulation systems, refractory protection systems, intumescent paint compounds, and water of hydration plasters. They surveyed the available literature in this field. While no data were available for LNG fire tests of these coatings, they felt that the existing data could be applied to LNG tanks and fires. One problem not completely covered in the literature was the effect of cryogenic thermal shock. They performed a small scale experimental program to test this using liquid nitrogen. Samples exposed to the cryogen showed effects varying with the primer used. Two coated samples were exposed to a Liquefied Petroleum Gas (LPG) torching impingment fire; one had been exposed to cryogenic temperature shock, and one had not been. They concluded that coatings gave a superior level of protection, but some coatings failed when exposed to liquid nitrogen (Wesson and Lott, 1977).

Fire protection is a major design and operating issue for land storage facilities. Passive protection should be given more attention in the future. Experimental testing of new fire extinguishing and fire control agents along with new methods of application can be expected. At the present time, though, there are sufficient data on which to base the design of facility fire protection.

III. WATER-SIDE RESEARCH

A. Ship Studies

Clearly one of the most important elements in the LNG industry is the LNG carrier. Not only are huge quantities of the cryogen carried at any one time, up to 125,000 m^3, but spills on water are, overall, potentially a more serious hazard than an equivalent spill on land. In order to develop technically acceptable and commercially viable ships, the various designers, builders, and supplier companies have necessarily undertaken extensive research and development programs. Such programs are required by the many regulatory agencies worldwide, as well. Unfortunately, most of this work remains proprietary. For this reason only a few research programs can be discussed here.

Most of these programs involve the LNG tank, which is reasonable since this is the most novel feature of an LNG carrier. Of particular interest is the spherical type of tank, one of the most popular designs in use today. The Moss-Rosenberg design for the spherical LNG tank has been discussed extensively in the open literature. One of the reasons for the wide-spread use of this design is that it can be thoroughly analyzed mathematically. Being essentially a simple shape, accurate analysis is possible, something that may not be feasible for the more complex designs. Howard of Moss-Rosenberg reported analyses performed on the Moss-Rosenberg sphere. Three related studies were performed. First, a complete mathematical analysis was undertaken, calculating the deflections of the tank under the various types of service loads. Then the fracture mechanics properties were developed experimentally, including such properties as critical crack lengths and fatigue crack growth rates. Finally, non-destructive tests were devised in order to set limits on the maximum size defects that could be present, undetected, in the tank at the time of delivery. The crack growth rates that were calculated demonstrated that before a crack grew to the critical length and the tank failed, the crack would be detected by the cargo leak detection equipment. Furthermore, the crack would propogate slowly so that there would be ample time to complete the voyage and offload the tank. Such tanks are of the "leak-before-failure" type and may be judged to be failsafe. Extra attention was paid to the equatorial ring, where the tank is connected to the supporting cylinder or skirt (the tank bottom does not contact the inner hull). During the hydropneumatic test of one of the tanks from the first of the Moss-Rosenberg 125,000 m^3 LNG carriers, the opportunity was taken to measure the stresses and strains as a function of fill volume and of time. These results supported the concept of "leak-before-failure." A comparison of the calculated stresses with the measured stresses showed reasonable agreement. A long-term, in-service test program was

begun on one ship; monitoring equipment was installed on the tanks and tank support structures. The intent was to monitor the tank for a time sufficiently long to gather data over a wide spectrum of sea conditions (Howard and Kvamsdal, 1977). In another report, Howard described the methodology developed for establishing the degree of sphericity of the tank. About 100 reference markers were precisely located by theodolites on the inner surface and about 1200 more were approximately located. Accurate location of the 1200 was accomplished by stereoscopic photography, and, with the 100 precisely located markers, photogrammetry. This method worked well. Also, he reported reasonable agreement between the calculated and measured stresses during tank hydropneumatic testing (Howard et al, 1977).

The U. S. Coast Guard, along with the U.S. Naval Sea Systems Command, the Maritime Administration, the Military Sealift Command, the American Bureau of Shipping, and the U.S. Geological Survey sponsor the Ship Structure Committee (SSC), with the participation of several other organizations. The emphasis of the SSC is on the improvement of the hull structure of ships. Three SSC projects involved LNG carriers. In the first SSC study the effects on a ship's hull given the catastrophic failure of an entire cargo tank were calculated. Sanders Associates, Inc. prepared the study, which is of great importance in evaluating the survivability of an LNG carrier after such a catastrophic incident. They developed a simple methodology for calculating the temperatures and stresses in the hull metal after tank failure. Small scale model tests were run and the findings generally agreed with the calculated predictions. Also considered were the dangers from tank overpressurization from the rapid vaporization of the spilled LNG in the inner hull space. They felt the ship would probably not survive (Becker and Calao, 1973).

Two further SSC projects involved research concerning damage to ships' cargo tanks from the acceleration forces produced by the tanks' cargo. If a tank is partially filled with LNG, and encounters a heavy seaway, some types of tanks could be damaged; this has happened in at least two instances. In the first SSC project, Southwest Research Institute compared the forces from LNG tank loadings to the then current (1974) rules established by eight agencies such as the Coast Guard, the American Bureau of Shipping, and Det Norske Veritas. Four different types of tanks and seventeen types of tank loadings and ship accelerations were considered in evaluating the eight sets of requirements. Finally, they prepared a set of model and full-scale tests to verify the ship motions used in these evaluations (Bass et al, 1976). The second effort, also by Southwest Research Institute, is a continuation of the previous effort, motivated by the sloshing damage occurring in slack loaded, membrane-type LNG carriers. This project is ongoing. The first of many parts is a

review of existing mathematical tank sloshing models, with model tests scheduled to provide additional sloshing data. Model tests will also delineate the response of membrane-type tanks to these forces. From this they will prepare new methodologies for calculating sloshing forces and tank wall response. The final task is the preparation of methods for including LNG sloshing in designing LNG tanks and their supporting structures. This work is in progress.

Fire aboard ship is one of the most feared type of accident and, when carrying such flammable cargoes as LNG or gasoline, the seriousness of fire is even greater. Great progress has been made over the years in both preventing and combating LNG fires. Faced with this new cargo and with novel containment systems, the Coast Guard contracted with University Engineers, Inc. to study fire safety aboard LNG ships. They examined the range of possible LNG spill volumes and selected the maximum extinguishable spill size; larger spills can not be extinguished by present equipment and methods. They evaluated how to extinguish the maximum extinguishable fire and what equipment was necessary. This evaluation was compared with the regulations imposed by the Coast Guard and by the Inter-Governmental Maritime Consultative Organization (IMCO). They considered the effectiveness of additional ways to reduce the damage from fire such as spill containment, water spray, and inert gases. Through fault tree analysis the relative risk of fatality was estimated for both the LNG carrier and for transfer operations. The total risk was expressed as a chance greater than 1 in 10^{10} of a fatality for each man hour of exposure. A figure of 10^{10} is typical of natural disasters. Interestingly, the risk from transfer operations was greater than that from the LNG carrier alone (Welker et al, 1976). A second part of the University Engineers' work involved a series of small scale tests simulating LNG spills and LNG spill fires, conducted in a 3 m by 3 m pit. Although the major effort was in providing data for scaling LNG tests to be run in the future, one group of tests simulated fire fighting aboard ship, where questions had been raised as to whether obstacles such as pipes within the fire might increase extinguishing time and the amount of dry chemical extinguishing agent required. Tests with obstacles showed that as long as the dry chemical can cover the entire surface of the fire, its effectiveness is not reduced. A test series using water spray and water fog to reduce the thermal radiation flux striking a surface showed that these techniques were marginal at best, that a better use of the water is direct impingement to cool the surface to be protected (Brown et al, 1976). This is of importance because water spray is required aboard LNG carriers to protect exposed portions of the tanks and the accommodation spaces. Direct impingement permits the full use of the water's sensible and latent heats.

Survivability of an LNG carrier when its hull is exposed to fire is very important. A fire caused by a release from one LNG cargo tank or by a release of another flammable

liquid from another vessel is serious enough; if the entire LNG carrier is lost, the problem is compounded. Authen and Skramstad of Det Norske Veritas examined this survivability issue. Their thermal analysis considered a fire along one side of a carrier's hull; many simplifying assumptions characterizing the fire were necessary in order to solve the problem. A method for calculating the temperature of the inner and outer hulls was presented. Both the membrane and the independent spherical type tanks were considered and scenarios presented for each type, both for cases when the tank fails and for cases when the tank survives. They presented several suggestions for increasing the chances of ship survivability such as water ballast in optimum locations and water spray on the deck and outer hull. While no answers were given as to the actual chances of an LNG carrier surviving such a fire, the study did point the way towards future work (Authen and Skramstad, 1976). Hopefully, answers will be forthcoming on this most important topic.

Liquefied gas ships, especially LNG carriers, must meet rigorous design requirements, including the ability to withstand low temperatures. Hulls are subject to brittle fracture, and conventional oil tankers have suffered damage from low ambient temperatures; with LNG service from Alaska, this problem looms large. Hicks and Henn of the Coast Guard analyzed the ambient air and water temperatures as a function of the month for twelve U. S. ports. They sampled the historical weather record and gave low temperatures for each port for each month. For service to U. S. ports, they recommended designing ships to the following design ambient temperatures; Alaskan ambients, five knots air at -29°C, and still water at -2°C; lower 48 states, five knots air at -18°C and still water at 0°C (Hicks and Henn, 1976).

If an LNG carrier becomes stranded or otherwise immobilized, offloading the cargo can be difficult. Since the operational boiloff is typically less than 0.25% of the cargo volume per day, lightening a ship through normal boiloff would require an extensive amount of time during which the ship itself might be a hazard. Offloading into another vessel is not as easy as with conventional tankers, due primarily to the scarcity of suitable receiving vessels. Some ships have a jettisoning capability, yet there are questions about the safety of such equipment. Jettisoning equipment was installed on one group of seven 75,000 m^3 vessels, and full scale tests were run on the GADILA, as described by Kneebone of Shell. Five tests, ranging in size from 27m^3 to 198m^3, were run. Variables included vessel speed, wind speed, and jettisoning rate. No large electrostatic fields were generated, and the vapor cloud did not threaten the vessel; vapor plume dimensions were measured. Finally, a series of recommendations was developed for safe jettisoning (Kneebone and Prew 1974, and Prew, 1976). A cargo transfer capability similar to that used to salvage conventional petroleum

cargoes might be superior, however. Until such a capability is available, jettisoning is a reasonable alternative.

New cargo containment systems are presented yearly. Of particular interest to the industry are those systems that do not contain a metal primary barrier. One group of these systems, the wet wall type, has LNG directly in contact with the insulation. None have as yet been placed in LNG service, and there are questions as to the consequences if the system failed locally and LNG contacted the inner hull. One study in the open literature, by Metz, considered this problem. He first developed a casualty scenario and then identified the critical structures in the ship's inner hull; the sudden contact of ambient metal with cold LNG produces stresses which may accentuate the existing stresses present in ships. Flaws present in the inner hull prior to the failure of the wet wall system could be magnified and conceivably lead to failure. Small scale tests were run to test whether critical portions of the inner hull would fail. The results from the thermal stress analysis and the small scale tests showed that carbon steel stiffeners and webs might require improvement. The cold surface of the inner hull would not fail, with or without pre-existing cracks (Metz et al, 1975). This type of analysis may well be applicable to other containment systems.

While it is important to develop the safest ship possible, it is also important not to ignore the human factor in vessel operations. Even if an LNG carrier could be designed and built so that no failure was possible, human error could lead to problems. The firms Operations Research, Inc. and Engineering Computer Optecnomics, Inc. studied the tasks performed by shipboard and terminal LNG personnel for the U.S. Coast Guard, and prepared guidelines for crew training and crew licensing for both ships and unmanned barges. Due to the limited operating experience with LNG shipping at the time the study began, the task analysis technique called Functional Job Analysis was modified for this purpose. Here the "job" is reduced to individual tasks and each task is studied for its proper level of required training and licensing. For example, one of these tasks is to "monitor the exiting gases in order to assure that the oxygen level is less than 2% by volume prior to starting tank cooldown spray operations," which is far removed from the usual job description for a "chief mate." A sequence was developed for training crewmen from shore based instruction, to provisional licensing, to the final full licensing; in particular, on-the-job training was deemed insufficient. License renewal would not be automatic; a recent LNG voyage would be required or recent shore based training. They concluded that all crew members should be taught the properties and hazards of LNG, even those who would not likely come in contact with LNG (Porricelli et al, 1976). Training and the human factor are important in all phases

of LNG transportation and yet little has been discussed about this important subject in the literature.

After all has been done to insure maximum levels of safety in vessel design and in crew training, there will still be "problems." In order to improve the safety record of LNG transportation by water, knowledge of all "problems" should be available to the industry. While this may not be the usual practice due to considerations of law, insurance, and corporate security, the LNG industry is so relatively new and a major accident would be so serious that an exception should be made. De Frondeville has prepared a record of the experience of LNG vessels plus a description of the various tank designs, vessels, and trades as of the date of publication, 1976. He considered the shore terminals, liquefaction trains, storage tanks, and peak shaving facilities. De Frondeville proposed the formation of a "reliability information bank" and, by implication at least, one for safety as well (De Frondeville, 1977). De Frondeville's work is as high in quality as it is in importance; the approach is extremely broad and covers all facets of the industry but, undoubtedly, it is far from complete. All involved, industry and the public, would benefit from an interchange of data on "what went wrong" as well as "what went right." The industry and the regulatory authorities are well aware of the Cleveland, Ohio tragedy in 1944, and are doing all that is possible to avoid any such disaster. Full disclosure of all incidents, however small, would be of help.

The LNG carrier has had an enviable safety record. Nevertheless research is needed to learn how a vessel will respond to a cargo release and to a large fire, and the ways to reduce the resulting damage. Full disclosure of operating problems will be of great help in increasing safety.

B. Flameless Explosion

One of the more spectacular aspects of the LNG safety research effort occurred when workers at the Bureau of Mines poured LNG onto a small aquarium partially filled with water. This was part of their project to measure the vaporization rate of LNG on water. Many such spills had been performed before, uneventfully. Suddenly there was an explosion, destroying the aquarium; there was no fire. Larger spills on a large pond were scheduled next, as part of the investigation of LNG vapor dispersion. Again, the work went forward without incident, until, after several spills, there was a large explosion just as the LNG struck the water. Again, there was no fire. While there was no instrumentation to measure the strength of the explosion, it was estimated to be equivalent to a "stick of dynamite." There had been small popping sounds noticed before, attributed to cryogen boiling inside an encapsulating ice layer. There was, however, no immediate explanation for the more violent phenomenon (Burgess et al, 1970). Apparently, this was not the earliest incident of an LNG Flameless Explosion (FE). During the 1956 tests for the Constock project, LNG was continuously poured onto the Bayou Long waterway in Louisiana for several days. A few FE's were observed. Many other cases of LNG FE's have been recorded (Enger and Hartman, 1972). The Bureau of Mines tests, however, appear to have precipitated interest in FE's.

If the flameless explosion could scale-up in violence with quantity spilled, there could be major questions in transporting LNG by water or even in storing it near a body of water. Fortunately, FE's did not occur every time but the very randomness and apparent irreproducibility seemed to underscore the danger.

Currently, the flameless explosion phenomenon is explained in the following manner. Consider a cold liquid on a warm solid. There are four boiling regimes in such a situation. For low temperature differences between the liquid and the solid, natural convection and conduction occur. As the temperature difference increases, nucleate boiling begins, with heterogeneous nucleation being provided by all but the cleanest, smoothest surfaces. As the nucleation rate increases with the temperature difference, an unstable transition regime ensues until, with the temperature difference sufficient, film boiling begins. Since the vapor film acts somewhat as an insulator the heat flux is actually greater for nucleate boiling prior to the transition boiling temperature regime in which the flux declines to film boiling. With a liquid boiling on a clean liquid surface, nucleation must be homogeneous. What appears to be happening with LNG after it is spilled on water is that it begins in the film boiling regime. As the methane component is preferentially vaporized, the temperature difference

declines and the transition regime is entered. The vapor film collapses and the two liquids come in intimate contact. Some hydrocarbon mixtures, including some aged commercial LNG, are already in the transition regime when spilled on water. The cryogen, due to a lack of nuclei, begins to superheat. The limit of superheat, or the greatest amount of heating that the cryogen can withstand before vaporizing, eventually is reached. For those warm liquids that freeze in contact with the cryogen, no FE is possible due to heterogeneous nuclei present on the solid. Similarly, an FE cannot occur when cryogen contacts warm solids initially. Once the limit of superheat is reached, an FE occurs. Some of the release of the superheat energy goes into the latent heat of vaporization and some into sensible heat. The volume increase occurs so rapidly that an "explosion" occurs. This is a non-chemical reaction; substances such as liquefied nitrogen could undergo FE's as well as hydrocarbons.

There are basically two theories of the limit of superheat, the thermodynamic theory and the kinetic. In the thermodynamic theory, the concept rests on the relationship $(\partial V/\partial P)_T$. When this equals zero, the limit of superheat is reached; for real spills on water the pressure is necessarily ambient. Note that $(\partial V/\partial P)_T$ should be less than zero, but it cannot realistically be positive. Since the region about the superheat limit is metastable, the physical property data are poorly understood. Accurate calculation of the term $(\partial V/\partial P)_T$ is therefore not possible. The calculation for mixtures such as LNG is even more complex. The temperature corresponding to the limit of superheat at one atmosphere is a fraction of the critical temperature. Depending on the equation of state used the fraction is either 0.84 or 0.89 of the critical temperature. The kinetic theory rests on the concept of the rate of homogeneous nucleation varying as a function of temperature. For pure liquids near the limit of superheat temperature, the rate of nucleation increases by orders of magnitude for each degree of temperature increase. Calculations cannot give the actual limit of superheat but can give a temperature range over which the nucleation rate is sufficient for vaporization. Apparently, Flameless Explosions have occurred many times in other areas, such as pulp mill smelt and water, nuclear reactor molten metals and water, molten aluminum and water, and molten steel and water. Water, of course, need not be the warm fluid. An excellent exposition on this may be found in Reid, 1976.

Garland and Atkinson of the University of Maryland experimentally investigated the FE phenomenon for the U.S. Coast Guard. Their LNG was liquefied from laboratory gas which was about 95% methane. Small quantities were spilled on water without producing an FE, and also onto twelve pure liquids or liquid mixtures, again without an FE. Pouring LNG onto water with a 1 mm hexane film or toluene film produced an FE each time. The rise in

pressure due to the FE ranged from 2 atm to 8 atm. Removing some of the high boiling constituents from the LNG reduced the likelihood of FE's. Further tests in which FE's were produced using 10-100 ml of LNG showed no correlation in overpressure with cryogen volume, but the pressure rise seemed to increase with the volume of the hydrocarbon on which the cryogen was spilled. Finally, repeated spilling of the same volume of LNG onto the same sample of hexane produced increasing overpressures. They concluded that the FE was a serious LNG hazard (Garland and Atkinson, 1971).

Burgess continued his study into this problem. He considered three possible mechanisms, ice encapsulation, clathrate formation, and superheating followed by rapid vaporization. Attempts to encapsulate LNG proved difficult, and the time required to form methane - water clathrates in the laboratory proved too long to be the cause of the phenomenon (Burgess et al, 1970). A later effort by Burgess was no more effective in rapidly generating methane - water clathrates. Test pourings of LNG onto a layer of pentane and hexane on water produced explosions as did mixtures of LNG on pentane and hexane. Several mixing tests of LNG with propane produced only one weak FE. Propane and hot (68°C) water were very effective in generating FE's. He did feel, though, that the methane concentration was very high when the two FE's occurred in the first study. A unified theory of this phenomenon was not developed at this time (Burgess et al, 1972).

Shell Pipe Line Corporation of Houston, Texas, conducted an extensive program of spills of hydrocarbons on water. In some 235 spills into a confined container, three types of responses were noted: for LNG spills sufficiently large, a coherent ice layer formed, but no FE's; for smaller sized spills, a partial ice layer prevented all but "popping" noises; for even smaller spills, no ice formed, and sometimes FE's occurred. Other liquefied gas mixtures were spilled onto water or onto other warm liquids; the temperature of the warm liquid was varied. Results indicated that for various mixtures of methane, ethane, propane, and n-butane, none would exhibit FE except where the methane concentration was below 40%. This is important, for most commercial LNG has methane concentrations between about 90% and 99%, except for Lybian LNG, with methane amounting to less than 70%. Aging of LNG in storage tanks was measured; calculations based on the assumption of methane being the sole component of the boiloff gave conservative, but approximately correct, values of the methane concentration versus liquid fraction boiloff. The tank contents had to be aged to 10% or less of the initial volume before the methane concentration could fall below 40%. Aging during the vaporization was also possible, that is, most of the LNG could boil away, leaving a methane-deficient cryogen on water. Calculations suggested that only spills of greater than 114 m^3 could possibly undergo FE. Of course, even after the cryogen had

reached the proper concentration, it would have been spread over a wide area and its potential for doing shock damage would be limited, particularly since it was improbable that the entire remaining liquid would reach the limit of superheat simultaneously (Enger and Hartman, 1972). This work by Shell Pipeline is the most extensive done in this area. They conclude that the danger is low.

Reid of the Massachusetts Institute of Technology has done extensive work in this area. His experiments were with various cryogens (liquefied methane, nitrogen, ethane, pipeline gas, and synthetic LNG, a mixture of propane and methane). He spilled these cryogens on water, spilled water on cryogens, spilled cryogens on ice, plus several other variations. One of the most interesting variations was the use of a hydrocarbon film between the spilled cryogen and the water. He hypothesized that two conditions were necessary but not sufficient for an FE, that the interfacial liquid must wet the cryogen and that the warm liquid must have a low freezing point (Nakanishi and Reid, 1971). This work suggests that the interface between the cryogen and the adjacent layer is all important, whether or not that adjacent layer is only a film.

In one series of tests, Reid observed the release of liquefied pipeline gas on water coated by n-hexane from below; initially the cryogen was separated from the n-hexane by a film of vapor. Suddenly the cryogen spread out and contacted the n-hexane surface. An FE followed. In a similar test the water temperature was monitored 3 mm below the n-hexane-water interface. The temperature decreased immediately after spillage but recovered rapidly; then it fell slowly until, over a period of less than 0.4 sec it fell 25°C and an FE occurred. This suggested a cryogen superheat of roughly 35° to 40°C. (Nahanishi and Reid, 1971). These results, though qualitative, do support the theory of the limit of superheat. Perhaps the existence of a hydrocarbon film could explain the FE's observed by Burgess when LNG (whose methane concentration was greater than 40%) was spilled on water. In a recent report, Reid discussed some 150 impact tests in which pressurized nitrogen provided the force for impacting the cryogen into the warm liquid. The higher the initial impact velocity, the greater the measured overpressure when FE's occurred, with overpressures as high as 13.6 atmospheres. Also, impacting the cryogen into the warm liquid allowed some pairs of cryogen and warm liquid (e.g., ethane-water) to undergo FE whereas spilling the cryogen did not. Methane, however, did not undergo an FE when injected into water (American Gas Association, 1977).

Reid reported on the phenomenon of superheated liquids and how they relate to FE's in a recent review paper. Examining homogeneous nucleation theory, he arbitrarily defined the

homogeneous nucleation temperature, T_{SL}, as corresponding to the temperature at which a million vapor embryos form every millisecond for each cubic millimeter. This temperature is usually within a few degrees of the limit of superheat, a good agreement, he felt, when the many approximations were considered. He surveyed past FE events and the various explanations advanced to explain these events. When cryogens are spilled on water, for an FE to occur, the warm liquid temperature, T_W, must be close to or greater than T_{SL}. When T_W is only 4% to 6% greater than T_{SL}, the probability of an FE is the highest. For all warm fluids T_W must be close to or greater than T_{SL}; for the greatest probability of FE, the ratio T_W/T_{SL} is somewhat above 1.0, depending on the warm fluid. Now for pure liquefied methane spilled on water the value of T_W/T_{SL} is 1.77, much too high for an FE. He suggested that if the cryogen were injected at a sufficiently high velocity, the vapor layer from the stable film boiling might be stripped from the interface, resulting in intimate contact between layers, followed by an FE. Ethane poured on water has never undergone FE's, but with the impact technique, it did. After reviewing the many theories, Reid concluded that there is not enough evidence to prove one mechanism for all FE's (Reid, 1977).

Porteus and Reid provided a very useful compilation of spills of pure cryogens on water, along with binary mixtures of cryogens on water. (Porteus and Reid, 1976). This is the most complete collection of FE data available in the open literature.

Probably the most detailed examination of the thermodynamic model of the FE is provided by Rausch and Levine. Their model predicts behavior only at atmospheric pressure. When the interfacial temperature is about 84% of the critical temperature, a shock wave will occur. For water-cryogen systems, the water temperature must be about 110% of the cryogen's critical temperature; much greater temperatures than 110% were predicted not to lead to shock waves. They performed a series of experiments using Freon 12 on water, Freon 22 on water, propane on water, and Freon 114 on ethylene glycol. Both the 84% and 110% values were closely followed; as predicted, both liquefied methane and liquefied ethane spilled on water failed to produce FE's. (Rausch and Levine, 1973). In a later paper they calculated the pressure of the shock wave based on theoretical considerations. Near the critical region the viscosity looms large in importance. Put colloquially, the energy transfer was increased due to the "squeeze" provided by the bulk viscosity. An involved procedure led to an estimate of about 34 atmospheres as the strength of a methane FE shock wave. Mixtures, of course, were not covered by their model but the authors felt the model might still apply. (Rausch and Levine, 1974). It would be useful to extend the work in their 1973 paper to the LNG (or liquefied methane) impacts on water, to calculate roughly the

velocity required for an FE. This could then be compared to the maximum possible pressures in land tanks and in ship tanks.

Workers at the Argonne National Laboratories performed a theoretical and experimental investigation into the FE phenomenon. Experimentally, water was injected into molten sodium chloride. The energy for the FE was either stored in the superheated liquid or was transferred across a very large interfacial area between the two liquids; that is, the cold liquid can fragment into small pieces with a much greater surface area. The experimental results, they felt, supported the idea of the fragmentation of the cold layer, but the exact mechanism was still unknown. The observed explosive energy was as much as 25% of the maximum theoretical energy available for the FE. Whether this fraction can be used with large LNG spills was not known. Finally, they suggested that submerged injection of LNG could be more hazardous than simple spills (Anderson and Armstrong, 1972).

Nelson worked in this area as well. He demonstrated that the LNG-water interaction is much less violent than the pulp mill smelt-water interaction. For the former, the immediate film boiling decays into superheating in the transition region, followed by the FE. For smelt dropping into water, the process of film boiling, superheating, and FE breaks the smelt into small parts, moving at a large velocity relative to the water. This favors intimate contact between the smelt fragments and water, followed by superheating and additional FE's. This chain reaction resulted in much greater damage (Nelson, 1973). Could this same type of chain reaction occur with LNG-water? There have been no reports of such chain reactions, but if large quantities of partially aged LNG were spilled, perhaps this mechanism might be observed. The fact that high pressure impacts seem to produce FE's when they do not occur with simple spills suggests that this mechanism might have some validity in large LNG spills.

Witte and Cox of the University of Houston investigated the phenomenon of Flameless Explosions on a theoretical basis. While they accepted the concept of super-heating, they added the idea of fragmentation in a manner similar to Nelson's. Basing the fragmentation mechanism on the molten metal-water and molten salt-water events, they proposed that LNG droplets were encapsulated in ice layers, pressurizing the LNG vapors. This was their explanation for the observed poppings. Three candidate mechanisms for fragmentation were rejected as a result of molten metal tests in water:violent boiling, cold liquid trapped inside a shell of the warm liquid, and Weber Number instability, the last a measurement of the inertial forces on the warm liquid falling through the cold liquid overcoming the warm liquid surface tension. Fragmentation was then triggered by other droplets fragmenting. They did not settle on a fragmentation mechanism (Wittle and Cox, 1971).

Opschoor of the Central Technichian Institute TNO (The Netherlands) performed a theoretical study of the LNG-water interaction followed by a review of the experimental tests. He accepted the thermodynamic model of superheat and through superheat energy transfer calculations estimated the mechanical energy of the LNG-water FE as being about 1.2 J/cm^2. He added that the Rausch-Levine estimate of overpressure was too large. He felt that only minor damage is possible to nearby structures when LNG spills on water (Opshoor, 1974).

In the early 1970's, the Coast Guard was very much concerned with this phenomenon and so requested the National Academy of Sciences Committee on Hazardous Materials to examine the issue. Katz, of the Committee, prepared a state-of-the-art review in 1972. Although somewhat dated, the conclusions reached then are still valid; liquefied methane will not undergo an FE when spilled on water and LNG will have to be aged drastically, either vaporizing in the storage tank or boiling on water before it will undergo an FE (Katz, 1972).

It is now known that, compared to combustion, the flameless explosion phenomenon is but a minor hazard. This is not to say that the work performed was fruitless, for it was this work that provided the evidence for discounting the problem. Unlike most other LNG research issues, the FE is important in other areas, including the pulp, the nuclear power, and the metallurgical industries. The large scale tests proposed by the U.S. Department of Energy will provide data on the aging that occurs during the boiling process on water. The question of whether the injection of liquefied methane or of LNG (of commercial concentrations) into water might produce an FE requires more work to answer. It is worth noting, however, that all portions of the LNG storage and transportation system are carried out near ambient pressure; it is difficult to postulate situations where LNG could be pressurized without rupturing its container. In summary, then, this problem has been solved insofar as ensuring an acceptable level of safety.

C. Dispersion From Spills On Water

How LNG behaves when spilled on water has been of great interest to all concerned with LNG importation by ship, particularly the maximum distance an unignited cloud might travel downwind and still remain flammable. Also of major importance is the problem of pool and cloud fires. There are several steps to the downwind dispersion problem, some of which apply to the fire problem. These include the pool spread rate and the vaporization rate per unit area as a function of time (including the question of the formation of ice), the buildup of an inventory of vapor above the pool, the gravity-induced spreading of this inventory, the rate of dispersion, and the significance of pockets of vapor whose concentration is greater than average. Not all of these steps are necessarily significant or even exist in actual releases.

Burgess of the U. S. Bureau of Mines studied this problem for the U. S. Coast Guard beginning in 1968. Small quantities of LNG were poured onto a water-filled aquarium mounted on a load cell in order to determine the vaporization rate. Next, larger quantities of up to 0.5 m^3 were spilled onto a pond. These spills were essentially instantaneous. An overhead camera gave data on pool spread rates and showed that no coherent ice layer was formed. A coherent ice layer could reduce the vaporization rate significantly and, therefore, the downwind travel distance. Hydrocarbon sensors gave data on the dilution of the vapor cloud. Burgess concluded that the vapor cloud, in effect, provided its own thermal inversion, which led to rather long flammable vapor cloud travel distance predictions. Also important was his finding of significant peak-to-average ratios of the vapor concentration. The thermal inversion or layering was explained by saying that the vapor cloud did not warm significantly from contact with the water below or warm from the sun, but only by mixing with ambient temperature air. Necessarily, this meant that the diluting air was cooled, so the vapor air mixture remained heavier than pure ambient air. Burgess' predictions came from a model based on the Gaussian plume dispersion. Surprisingly, the data suggested significant pockets of vapor whose concentration was heavier than average, so the distance downwind for which the cloud remained flammable should not be calculated to the lower flammable limit, but to a much lower concentration. The pool spread data suggested that the rate of spread was constant (Burgess et al, 1970). In a follow-up effort, Burgess generally confirmed his earlier spill results. Spills of a continuous type were used this time, with the quantity of LNG released being about 10 m^3. Again, his model based on the test results gave long downwind cloud travel distances (Burgess et al, 1972). These data were surprising. Prior to these studies, it was thought by many that the cryogen would cause the

water directly underneath to freeze, resulting in a vaporization rate per unit area that would drop with time. Also, since methane vapor at ambient temperatures is lighter than air, it was believed that it would rise rapidly from the boiling pool. Since both ideas were incorrect, the downwind hazard zone is much greater than considered previously. This motivated further research.

May, of ESSO Research & Engineering Co., conducted a series of seventeen LNG spills at Matagorda Bay, Texas, ranging in size from 0.73 m^3 to 10.2 m^3. This work was part of the American Petroleum Institute's LNG spill study. The larger tests were classified as being intermediate in LNG spill time, rather than instantaneous or continuous tests. May found the same type of vapor layering and lack of ice formation as in the Burgess tests, but with a lower peak-to-average ratio of vapor concentration. The spills led to a new model in which the boil-off vapor did not immediately take on the wind velocity, but rather built an inventory above the pool which underwent a gravity spread phase, followed by a vapor dispersion phase. A series of point sources arrayed in a line accounted for the rather large diameter cloud, and from each point, dispersion was modeled as a Gaussian dispersion. The downwind distances predicted were generally less than those given by the Burgess' model (Feldbauer et al, 1972).

Boyle and Kneebone of Shell Research Limited conducted a series of small scale laboratory tests of LNG spillage on water. This was also a part of the American Petroleum Institute's research work on LNG-water spills. They measured the evaporation rate on water to be 0.024 kg/m^2 sec; if ice formed, this rose to 0.20 kg/m^2 sec. The factors influencing ice formation were studied, ice having the effect of causing the boiling regime to shift from film boiling to nucleate boiling with an increase in boiling rate. The spreading rate of LNG was measured to be about 0.76 m/sec initially but it fell rapidly with time. The LNG pool on water broke up when the amount of LNG fell below 0.78 kg/m^2. Water was "picked-up" into the vapor cloud during the LNG vaporization process, as much as 8 weight percent of the LNG. Vapor cloud travel experiments were conducted in a wind tunnel; the cloud was in the shape of a wide, flat plume with a height to width ratio of 1:25 (Boyle and Kneebone, 1973). This work was quite comprehensive. Curiously, ice formation during water spills might have been expected to reduce the LNG vaporization rate as happens with land spills when the ground freezes. Burgess' test results showed less layering, with a ratio of only 1:5. Finally, the issue of water "pick-up," which can effect cloud density and vapor dispersion, has not been addressed by others.

Kneebone, of Shell Research Limited, described the jettisoning tests from the 75,000 m^3 LNG Carrier GADILA. In five tests from 27 m^3 to 198 m^3 of LNG were released. These remain the largest spill tests on water to date. Since the emphasis was on evaluating the safety of the jettisoning apparatus, the data were not as detailed as in other test series. Each test lasted for approximately ten minutes, so each was of the continuous type of spill. The layering in this series was greater than that observed by Burgess, with the ratio of the vertical dispersion rate to the horizontal being 1:25 in place of Burgess' 1:5; the latter is also the ratio found during thermal inversions. Complicating the issue was the fact that some of the LNG vaporized before reaching the water. Kneebone said that for his larger spills, the data correlated well with the model by May. Parenthetically, it is worth noting that the jettisoning system performed well (Kneebone and Prew, 1974).

The Japan Gas Association performed a series of spill tests for the Japanese Government at the Sodegaura terminal of the Tokyo Gas Company, Ltd. One test included pouring LNG onto water in a diked area. This technique was novel, for the problem of determing the pool area as a function of time was circumvented by using a dike; the water did not freeze during the course of the experiments. As expected, no flameless explosion occurred since the methane concentration in the LNG was over 99%. The dispersion coefficients and the concentration profiles did not markedly differ from those measured in land spills (Japan Gas Association, 1976).

Lind, of the Naval Weapons Center, China Lake, California, is performing dispersion tests as well as cloud and pool burns of LNG spills on water. While all experiments are not yet complete and the results obtained have not been completely evaluated, there is the qualitative observation that there is an ice-like white solid material formed. Further study of this ice-like material is scheduled. The spill size was under 5.7 m^3 onto a pond 50 m by 50 m and about 1 m deep. No reports are as yet available.

The U. S. Department of Energy has published an assessment indicating a need for further LNG research. While the complete program has not been adopted or funded as yet, if implemented, it will have a significant impact on the spill problem. The cornerstone of the plan and the bulk of the budget lay in three series of spill tests, small, about 5.7 m^3 (ongoing at China Lake), medium, about 40 m^3, and large, perhaps 1000 m^3. The 1000 m^3 tests would have a release time of several minutes, probably being classified as an intermediate spill rather than an instantaneous spill. The proposal includes a comprehensive program of instrumentation development and test facility construction (U. S. Department of Energy, 1978).

Questions still remain about the length of the downwind hazard zone. The main question is usually phrased as, given a maximum credible spill involving an LNG carrier, how far can the cloud travel and still be flammable? The maximum credible accident probably was first defined by the U. S. Coast Guard as an instantaneous release of the entire contents of a single tank in the largest LNG carrier. This volume is given as 25,000 m^3, one of five tanks in the 125,000 m^3 ships (U.S. Coast Guard, 1976). An instantaneous release, though probably not very realistic, was chosen for want of a more realistic release rate. Since large-scale spill tests are so expensive and so difficult, many have attempted to model the phenomenon directly without new spill tests. Havens has analyzed some seven models for the U. S. Coast Guard, including the Burgess and May models discussed above (Havens, 1977).

The following discussion is based on Havens' analysis. The seven models differ significantly. For example, the Burgess model employs a simple Gaussian dispersion from a point source without a gravity spread phase or correction for the pool area. The May model uses a multiple series of phases - vapor build-up over the LNG pool, gravity spread with air entrainment, and a series of point sources arranged in a line to simulate the large vapor cloud. The Germeles model is a Gaussian dispersion from a point source corrected for the pool diameter. In an earlier step, there is a gravity spread phase incorporating air entrainment. The Coast Guard model, developed by Arthur D. Little as a part of the emergency response tool, the Chemical Hazards Response Information System (CHRIS), is a Gaussian dispersion from a point source corrected for the pool diameter but without a gravity spread phase. The Fay model uses a relationship based on the Gaussian dispersion from a point source with no correction for an area source; there is a gravity spread phase with no air entrainment. The Federal Power Commission (FPC) model is somewhat different. The vapor forms a cylinder above the pool, with the diameter of the cloud being equal to the maximum pool diameter. The cloud then undergoes a gravity spread phase without air entrainment. Movement of the vapor from above the spill site is governed by heat transfer from the air; the vapor then undergoes a Gaussian dispersion from a point source with a correction for an area source. Finally, the Science Applications, Inc. (SAI) model is unique. It is a computerized model that uses a finite difference solution of the combined energy, mass, and momentum conservation equations. Gravity spread with air entrainment is involved. This model requires large amounts of computer time and is expensive to use. Havens categorizes the models as follows: The Fay, Germeles, and Coast Guard models are of the instantaneous vapor release or puff type; the Burgess, May, and FPC models are of the continuous vapor release or plume type; and the Science Applications, Inc. model solves the combined energy, mass, and momentum conservation equations. Table I is based on Havens' Table III-1.

TABLE I

Comparison of Predictions for a 25,000 m^3 Spill

Model		Downwind Travel Distance in km
Puff		
	Fay	20.8
	Germeles	18.5
	Coast Guard	26.2
Plume		
	Burgess	40.6-81.0
	May	8.37
	FPC	1.21
Combined Equations		
	SAI (Prediction for 37,500 m^3)	1.93

The above table gives the downwind travel distance for a 25,000 m^3 spill of LNG given the specific conditions, such as weather type, recommended by the model developers. The SAI distance is for 37,500 m^3. Havens noted that the distances change dramatically if other specific conditions are used. The problem with such predictions is that there are data for the small-scale spills for which the models are calibrated, but not for the larger spills. This means that the models agree generally for small-scale spills, but not for large-scale spills; furthermore, a plot of cloud concentration versus distance for a 25,000 m^3 spill shows that for a small change in concentration at the 5% or Lower Flammable Limit part of the curve gives a large change in distance. Havens is continuing his study of the Germeles and the SAI models. More theoretical and experimental work is needed before any one model can be used with confidence.

D. Underwater Releases

One area in which the entire known experimental record consists of a single test set is that of underwater release of LNG. An underwater release could occur due to striking an underwater obstacle; alternatively, a bulbous, projecting bow might puncture an LNG carrier below the waterline. Underwater release of LNG is important because an immediate ignition of the spill is less likely than if the release were at or above the waterline. How the vaporization rate would be affected is not clear, and how the LNG carrier would be affected is also unknown. Thus, the conventional models of vapor dispersion and the survivability of the damaged carrier itself are in question.

The aforementioned single test set was performed by Burgess for the Coast Guard. Five gallon (0.02 m^3) containers were submerged in about 3 m of water and explosively ruptured. Two tests were made and in both cases only vapor reached the surface, with no visible fog, as occurs when LNG is spilled on land or on water. This was interpreted as demonstrating that the LNG totally vaporized while underwater and that the vapor may have been warmed as well (Burgess et al, 1972). The more rapid vaporization from an underwater release could lead to a much longer downwind travel for the hazardous vapor cloud; however, if the vapors were warmed close to the water temperature, the downwind travel distance would be much less, as the cloud would be lighter than air at ambient temperature. Thus, the effect of releasing LNG under water is not really known.

Raj and Reid have theoretically analyzed the release of LNG below the waterline from an LNG carrier. Although there were other possible scenarios, they examined that of a jet of LNG into water. Unfortunately, there were little experimental data on which to base a model, but they prepared a model relating the size of the liquid slug to the rise time and percent liquid vaporized. The quantity of LNG vaporized increased with the fragmentation of the liquid jet. They also added that the calculated jet velocity and the liquid slug rise velocity were below the 20 m/sec velocity for which it is known that Flameless Explosions do not occur. (Raj and Reid, 1978). The problem of verification of this model and its underlying assumptions remains.

The tests by Burgess and the work by Raj underscore the fact that more experimental work is needed before the phenomenon of underwater LNG release is understood. No work is known to be in progress or planned in this area.

E. Water Spill Fire Studies

In the event of a collision resulting in a cargo release from an LNG carrier the most probable result would be a large pool fire rather than an unignited boiling pool giving rise to a vapor cloud. The argument usually advanced is that collisions sufficiently energetic to breach an LNG vessel's cargo tank will cause sufficient frictional heating and sparks to ignite the LNG vapors. Alternative sources of ignition are present on the LNG vessel or on other nearby ships. Experiments at China Lake and at the Bureau of Mines (Burgess et al, 1972) showed that vapor clouds burn back to their source, so that an understanding of pool fires is very important to LNG safety. Although this collision scenario can not be verified experimentally, the U. S. Coast Guard uses it (U. S. Coast Guard, 1976).

Usually the critical pool fire problem is stated in terms of the thermal radiation flux as a function of time for a given instantaneous release of LNG. This dynamic problem is more difficult than, say, a steady state release, but is a realistic statement of a worst case accident. Evaluation of this problem will help in deciding such issues as siting requirements. The instantaneous spill requires the determination of the pool spread rate, which is not well understood. While the LNG burning rate on water per unit area is known, assuming no ice forms, the pool area and therefore the total energy release rate are not well known. Furthermore, the peak thermal flux received by an individual or structure will be of short duration, requiring more information on the human response to thermal radiation which varies rapidly as a function of time. While much work has been performed LNG fires on land with their fixed area, the LNG fire on water has not received as much attention.

The Naval Weapons Center, China Lake, California, is performing a series of pool fires on water for the Coast Guard with financial assistance from the U.S. Department of Energy and the American Gas Association. No reports of this work are yet available. Quantities of up to 5.7 m^3 of LNG were released rapidly onto a water pond 50 m by 50 m, about 1 m deep. The spills were ignited either at the start of the spill or after some delay in an attempt to achieve a large pool diameter and hence a large fire. Theoretically, once an optically thick flame is achieved, no larger fire is necessary. Radiometer measurements were taken but the data are not yet available. Interestingly, an ice-like material was observed in the films of some of these tests; this is being investigated. Qualitatively the height to diameter ratio of the fire appeared to be significantly greater than the 3.0 or so observed in land LNG fires. In addition, the U.S. Department of Energy has proposed a series of large fire tests on water.

Theoretical analyses are useful, especially until the China Lake results are reported. Perhaps the first analysis was provided by Burgess when he took the burning rate per unit area of LNG on a frozen substrate (as would be the case in a land fire at steady state) and added to this rate the vaporization rate of LNG on water that he found experimentally. The sum was then the estimated burning rate of LNG on water per unit area. He assumed that, as an upper limit, 40% of an LNG fire's energy would be radiated outward. He modeled the fire as a point source fire, and calculated the radiation flux received at a certain distance from the pool fire center. The flux received was the total energy rate divided by the area of a hemisphere whose radius was the distance from the receptor to the pool center. The pool diameter and the burning rate gave the total energy release, and the former could be calculated by using his experimental data for unignited LNG pool size as a function of time and initial spill volume (Burgess et al, 1972). In the worst case the pool size could be calculated by assuming that the pool spreads without ignition until the maximum pool size is reached, and then is ignited. This model is not the most sophisticated but is conservative, simple to understand, and easy to use.

Raj and Kalelkar prepared a more complex model. They used a modified force balance oil spread model to predict the pool diameter as a function of time, allowing for the LNG to vaporize due to energy input to the pool from both the water and the fire. Another form of this LNG spread model was used in the Coast Guard's Chemical Hazards Response Information System vapor dispersion analysis. The time to burnout was calculated from the spread and liquid regression rates. The next step, the calculation of flame height, was difficult. Using land (diked) fires, where a ratio of height to diameter of 2.7 was observed, a ratio of 3.0 was picked to provide for large diameter spills, where, Raj said, most such ratios break down for other fuels. The flame was modeled as a tilted cylinder. The calculation of the radiation received involved evaluating the view factor from this tilted cylinder. Other terms such as atmospheric transmissivity and flame emissivity were treated conservatively. Raj presents a set of useful plots of maximum thermal flux as a function of distance and spill size. (Raj and Kelelkar, 1973). Note that the preliminary tests at China Lake suggest a height to diameter ratio greater than 3.0.

Stannard has developed a third model. He began with Burgess' spill spread model, adding a term representing Burgess' factor for the LNG burning rate on a frozen substrate. Stannard gave equations for the view factor for tilted and untilted cylinders, and calculated the receptor's subtended solid angle. From these equations he calculated the critical distances to human skin damage and pointed out that, since the maximum flux level is slow to build up, people will have time to escape from the fire. Although this method is less involved than Raj's, it is easier to use (Stannard, 1977).

The problem of calculating the thermal flux from pool fires is difficult. Until the results from the China Lake tests are in hand, questions will remain about the accuracy of the three models discussed above. Although it is the most complex, the Raj and Kelelkar model is probably the best to use today.

IV. RESEARCH COMMON TO BOTH SHORE AND WATER

A. Vapor Cloud Deflagration

It appears clear that the risk of an unconfined LNG vapor cloud detonating is not very significant, so the major hazard from such clouds is a deflagration or fire. The danger from asphyxiation and from cold "burns" is very low except, perhaps, near the spill site. Vapor cloud fires are a serious matter; one simple rule states that everyone within a deflagrating vapor cloud but outside a building or other shelter will die. Strehlow reviewed some 107 vapor cloud incidents from 1930 to 1972 not involving LNG plus the Cleveland 1944 LNG disaster. The overwhelming majority of these clouds deflagrated, not detonated. During this period about 386 died, 136 alone from the Cleveland LNG incident (Strehlow, 1972). Clearly cloud fire is a significant hazard, for under certain circumstances an LNG vapor cloud could drift a short distance into a built-up area and endanger life. There are two important issues to resolve, the level of the thermal flux from the fire and the ability of the flame front to travel upwind, that is, whether (and if so, how fast) the flame front will travel through the entire vapor cloud against the wind. Note that ignition is likely to occur near the leading, downwind edge of the cloud.

Lind, of the Naval Weapons Center, China Lake, California, is performing work sponsored by the Coast Guard, with financial assistance from the American Gas Association. Here up to 5.7 m^3 of LNG are released into a pond of water 50 m by 50 m and about 1 m deep. The release is as rapid as possible. The LNG is allowed to vaporize and the vapors drift downwind with flares igniting the cloud some distance from the pond. While there are no reports of this work, preliminary (and qualitative) results of these 1977 and 1978 tests indicate that the flame front can propagate upwind. After correcting for the wind velocity, the flame speed appears to be of the same order as that found in his hemisphere tests (see Lind et al, 1977) for the results of the hemisphere tests). Radiometer data are not yet available. The flame propagation is quite similar to the qualitative results found by Burgess during a test in which a continuous LNG release on water was ignited downwind. The flame front advanced slowly upwind to the source. No radiometer data were taken (Burgess et al, 1972).

Hardee et al, of Sandia Laboratories, considered the hazards from LNG fireballs. They postulated three types of fireballs, a premixed cloud that burned as a fireball, a pure fuel cloud that burned as a turbulent diffusion flame, and a fire that overpressurized an LNG

storage tank, causing it to rupture and form a fuel/air cloud. Hardee developed models for the first two cases. Optically thin methane fireballs, both pure and premixed, were produced. These included pure methane fireballs of 0.10, 0.15, 1.50, and 10.0 kg, and premixed stoichiometric fireballs of 1.5, 3.5, and 10 kg. The surface thermal radiation fluxes measured led to an estimated optically thick premixed fireball surface flux of 469 kW/m^2. Comparison with the Cleveland, Ohio, 1944 LNG disaster showed reasonable agreement with this estimate. They concluded that large LNG fireballs could lead to third degree burns at a distance of several miles from the fireball center (Hardee et al, 1978). This flux of 469 kW/m^2 is several times greater than the 100 kW/m^2 recommended for deflagrating LNG pools by Raj. This indicates the greater danger from a fireball relative to a simple pool fire.

Whether the LNG is initially spilled on land or water does not matter significantly for cloud fires, because the radiation from a vapor cloud fire should be the same for a given size cloud. Due to the uncertainties involved in predicting the vapor cloud dimensions and local concentrations as the cloud drifts towards an ignition source, precision in the description of the thermal flux from a burning cloud is probably not needed. Two researchers have developed models of cloud burning, Fay's fireball model and Raj's more conventional "wall fire" model.

By analogy with observations of cryogenic fuel releases and the resulting fires from the space program, Fay suggested that combustion of LNG vapor clouds would have the appearance of fireballs. He constructed a theoretical model in which certain scaling laws were established. The rise height of the fireball varied as the 1/3 power of the vapor cloud initial volume, the maximum flame diameter as the 1/3 power, and the combustion time as the 1/6 power. He then conducted very small scale tests with spherical soap bubbles filled either with pure methane, ethane, or propane. Hot wires ignited the spheres, which ranged in volume from 20 to 190 cm^3. His postulated scaling rules were confirmed (Fay and Lewis, 1971). There are some difficulties with Fay's fireball approach. LNG vapor clouds probably have a length to height ratio of 100:1 to 1000:1, rather than the ratio of 1:1 found in a sphere. Whether this LNG shape, resembling a thin pancake, could form a spherical shape as in a fireball is unclear; no mechanism for this has been advanced. Also, the soap bubbles of fuel are not premixed with air, whereas the vapor cloud is likely to have considerable air premixed. Finally, a fireball appears to require that the ignition spread more rapidly around the air-fuel interface than through the bulk of the fuel. A realistic LNG vapor cloud is very thin and combustion is likely to occur through the cloud as well as along its edges. While the

China Lake tests have not supported Fay's model, it may be true that they are not sufficiently large to prove or disprove his model.

Raj and Emmons modeled a vapor cloud fire as a "wall fire," a two-dimensional fire that moves through the cloud perpendicular to the wind direction. He postulated one or more point ignition sources that coalesce into a wall of fire. The model assumes a wedge shaped burning region normal to the wind direction; the length of the wedge is the width of the cloud. The wedge is widest at the top of the vapor cloud and comes to a point at the bottom of the cloud. Once steady state burning is reached, the dimensions of the wedge should remain constant. Raj's model calculated the width of the wedge at the top of the cloud, giving the thickness of the flame. The height of the flame is related to this width and so the thermal radiation can then be easily calculated (Raj and Emmons, 1975). Raj assumed a pure fuel cloud, while in reality all classical Gaussian cloud models and experimental tests show a variation of hydrocarbon concentration as a function of location within the cloud. Burning velocities may then be expected to vary somewhat across the cloud's cross section, whereas Raj's model assumes the velocity not to vary. Until large-scale cloud fires are studied, it may not be possible to determine if the variation of the hydrocarbon concentration is significant.

The ability to calculate the thermal radiation from an unconfined vapor cloud has not been demonstrated. The results from the ongoing China Lake cloud deflagration tests will be helpful in evaluating these two models. Proposed experiments by the U.S. Department of Energy would help in this area, too.

B. Vapor Cloud Detonation

As serious as an unconfined (without walls) vapor cloud fire may be, an unconfined detonation of an LNG vapor cloud would be much more serious. Unconfined hydrocarbon-air detonations have an explosive effect equivalent to 5-15 times the hydrocarbon weight in TNT. Fortunately, assuming a Gaussian plume, only a small portion of an LNG vapor cloud is within the flammability limits, and even less is near stoichiometric. Burgess calculated that, at the most, only 10% of the cloud is flammable at any one instant (Burgess et al, 1974). Nevertheless, there is reason to ask whether LNG vapor clouds can detonate in the manner of Liquefied Petroleum Gas clouds. Defining the problem is, in some ways, difficult; due to the variation in concentrations of the components of LNG, it is not sufficient to ask whether methane detonates, but whether vaporized LNG detonates. The presence of hydrocarbons heavier than methane appears significant in producing vapor detonations. It has been established that pure methane can detonate in a confined space.

In order to study the behavior of detonating methane-air mixtures one must first achieve a propagating detonation. There have been no recorded cases of this occurring in accident situations. Previous tests have usually involved high explosives to initiate directly methane-air detonations rather than other mechanisms that might cause a deflagration to detonation transition (DDT).

Kogarko published work on the direct initiation of methane-air detonations (Kogarko et al, 1966). While he reported having achieved a methane detonation, his work has been critized as being of too small a scale to separate the effects of the initiator from those of the methane. Others have pointed out their inability to duplicate his results.

TRW conducted a series of spherical balloon unconfined detonation tests for the American Gas Association at the TRW Capistrano Test Site. Seven tests were run with a stoichiometric natural gas-air mixture, with the natural gas being about 88 percent methane. Five tests were run in 1.5 m diameter balloons, two in 6.1 m balloons, and one with an initiator but no fuel. The high energy initiator used was Composition 4, with weights ranging from 384g to 680g. The 6.1 m tests were sufficiently large to show that the detonation decayed as it passed through the cloud. This suggested that the 1.5 m diameter tests, which showed apparent detonation propagation, should be considered too small relative to the initiator charge. TRW concluded that the question of unconfined natural gas detonability had not been answered, and that further work was needed. (TRW, 1969).

Vanta, at Eglin Air Force Base, simulated an unconfined vapor cloud using a rectangular framework covered by a thin polyethylene sheet. Twice, natural gas was detonated by about 1.0 kg of high explosive, but the two detonations were said to be erratic. The detonation propagated the length of the available bag, four feet. Several other tests with less initiator and with more distance for propagation failed to detonate. (Vanta, 1973). While the shock wave seems to have propagated four feet, a major question is whether the shock wave could have propagated in a steady state fashion over a larger distance.

Bull, of Shell Research, Limited, experimented with the methane-oxygen-nitrogen system in stoichiometric proportions, where the nitrogen concentration was deficient relative to that found in air. He used polyethylene bags with a charge of tetryl placed either centrally or at one wall. He correlated the amount of tetryl required to initiate direct detonation with the ratio of diluent nitrogen concentration to methane concentration. The data gave a reasonably straight semi-logarithmic plot of the minimum weight of tetryl, a high explosive, to initiate detonation versus the nitrogen to methane ratio. Extrapolation of the line to methane stoichiometric in air suggested that 22 kg of tetryl should lead to direct initiation. One necessary requirement for such a test is a reasonably large bag so that the effects from the tetryl itself can be separated from those of the methane. Bull estimated this minimum propagation length as 11 m (Bull, 1976).

Boni, of Science Applications, Inc., performed small-scale tests with the methane-oxygen-nitrogen system, similar to Bull's, which gave similar results. He developed an involved computer simulation of this system, giving calculated minimum energies required for detonation. Computer simulation of this system was validated over the range of the experiments performed by Bull and Boni. Calculations for the direct initiation of methane-air indicated a requirement of an initiator of 1000 kg to 10,000 kg of tetryl, very much greater than Bull's 22 kg. This type of behavior, where a plot of explosive weight required for direct initiation versus the nitrogen-fuel ratio shows that the explosive weight sharply rises as the ratio approaches that of the fuel stoichiometric in air, is known experimentally with propane and acetylene. Also, his calculations show that an initiator too weak to cause a steady state propagation can, nevertheless, generate an erratic, unsteady pseudo detonation that will, after a short time, decay into a deflagration. (Boni, 1977). The estimated initiator required is much greater than that estimated by Bull.

Benedict, of Sandia, used a thin plastic sheet covering a metal framework to contain the fuel-air mixture. Detasheet, a sheet explosive, amounting to 3.6 kg in a 2.4 m square

rectangular column, was sufficient to initiate directly a detonation wave over the 6 m length of the column. A 4.1 kg explosive charge proved sufficient for a 12 m long column. Several other tests failed to propagate the full length of the experimental chamber, due either to lower explosive charge and/or smaller chamber cross-section. High speed photography determined whether the vapor-air mixture detonated. (Benedict, to be published). As always with tests of this type, there are questions about the distance the wave can propagate. Boni's pseudo detonation could be involved here too, since Benedict's high speed photography could not capture the stability of the shock wave.

Nicholls, of the University of Michigan, used a pie-shaped detonation chamber to simulate a segment of a spherical detonation. He, too, measured the initiator energy necessary for direct initiation of the methane-oxygen-nitrogen system, and plotted the explosive weight versus nitrogen-methane ratio semi-logarithmically. Extrapolation to methane-air gave a requirement of 535 g of Detasheet. In his plot, however, he found a region where the experimental results did not clearly indicate whether a propagating detonation occurred (Gabrijel et al, unpublished).

Lind, of the Naval Weapons Center, China Lake, California, has been working on unconfined vapor cloud explosions. His work differed from previous work in that he included DDT's as well as direct initiation with high explosive as the mechanisms for study. He used 5 m and 10 m radius plastic hemispheres mounted on a concrete pad. His first series of tests used very weak initiators, trying to see whether flame front accelerations could be produced either naturally or by turbulence-inducing obstacles. Neither methane-air, propane-air, ethylene oxide-air, butadiene-air, ethylene-air, nor acetylene-air showed significant flame front accelerations or overpressures. Some acceleration was noted in the vertical direction, probably due to buoyancy, and even more along the partially enclosed instrumentation channel in the concrete pad, but no significant acceleration occurred in the bulk of the cloud. Direct initiation by high explosive followed. In two tests in 5 m hemispheres, a stoichiometric methane-air mixture failed to detonate. The initiators were 1.35 kg and 2.05 kg of Composition B, a high explosive. Apparently heavier hydrocarbons are significant in producing vapor cloud detonation; stoichiometric mixtures of methane and propane in air showed different results when 2.0 kg of Composition B was used in 5 m hemispheres. For methane:propane ratios of 60:40, 70:30, and 85:15, a detonation was sustained while two tests at 90:10 did not (Lind, 1974, Lind and Whitson, 1977). Plans for the future include tests using an initiator energy greater than Bull's estimate of 22 kg of tetryl.

It is significant that most of the work has concentrated on high explosive direct initiation and not on other mechanisms. This is important to consider for it is not likely that detonating high explosives will be found in accident situations. More likely, sources of initiator energy are small enclosed spaces, long pipes, or conduits filled with a vapor-air mixture that detonate; how the surrounding unconfined vapor cloud will behave is not known. Furthermore, since boiling LNG will be almost entirely methane at first, then ethane, and then propane, the vapor cloud may well be almost entirely methane-air in one portion, ethane-air in another, and propane-air in a third portion. Whether a propane-air detonation could trigger a methane-air detonation is not known. Finally, a real cloud is not stoichiometric throughout, but rather is a non-uniform mixture of fuel and air. How far a detonation would propagate is not really known; thus, there are areas for future study. At this time, however, it is reasonable to conclude that an unconfined vapor cloud detonation following a massive LNG release is not likely.

C. Physical Properties

Physical property data is very important for many applications in the LNG industry. Accurate data is needed, for example, in the design and operation of liquefaction units, in undertaking the thermodynamic analysis of such physical behavior as the Flameless Explosion phenomenon, and perhaps most important of all, in custody transfer. Finance rather than safety is the principle reason to be concerned about custody transfer - LNG is usually sold by the energy content, within certain limits of energy density. Thus, a consistent error in the volume of liquid delivered or in the energy per unit volume could make a significant difference in the balance sheet, perhaps millions of dollars per year. While equipment is usually designed with sufficient margin to deal safely with errors in physical property data, the efficiency of this equipment might well be significantly reduced. Fortunately, much of the work done in recent years has been published in the open literature.

Physical property data for LNG is not easy to measure. Since LNG is a complex mixture of many components it is necessary to study the data as a function of composition. The temperature region of interest is near the mixture boiling point, not the easiest region to study. Also, LNG is hazardous at any temperature; any material at LNG temperatures is hazardous as well. Unlike most situations, errors of even 1% could be very costly, so extreme accuracy is important. Despite these difficulties, there has been significant progress.

The National Bureau of Standards (NBS) has been studying the physical properties of the components, much of which was funded by the American Gas Association (AGA). Some of the topics investigated include orthobaric density, calorimetric, acoustical, thermodynamic, dielectric, optical, viscometric, and thermoconductivity data. Pure compounds (the first five alkanes plus nitrogen), binary mixtures (such as nitrogen-methane), multicomponent mixtures (such as nitrogen-methane-ethane-propane) and commercial LNG compositions were studied. Parrish and Hiza studied vapor-liquid phase equilibria in the nitrogen-methane system between -153°C and -178°C, the triple point of methane and the critical point of nitrogen. This system was not only important industrially, but it was important in developing liquid mixture theory. Good agreement was found between their data and that of previous workers (Parrish and Hiza, 1973). They also worked with the four

methane binary systems with ethane, propane, isobutane, and n-butane, compiling some 130 isotherms of vapor liquid equilibria that had been published in the open literature. Using thermodynamic theory they found major discrepancies in these isotherms and recommended care is using such data (Parrish and Hiza, 1975).

The NBS work was not limited to physical property data; some research concentrated on volume flow rate and density measurements. Mann surveyed the NBS work in 1976. A large flow measurement facility was built to test many kinds of flow meters. Thermophysical property data for the LNG components and mixtures permitted accurate determination of densities. These known densities could then be used for measuring the performance of existing densimeters, some of which were accurate to within less than 1%. (Mann, 1976). A useful source of information on the NBS' activities is their semi-annual report, "Liquefied Natural Gas Research at the National Bureau of Standards," Boulder, Colorado.

Air Products and Chemicals, builders of LNG liquefaction plants, is concerned with developing physical property data, including the solubility of solid compounds in liquefied methane as a function of temperature and pressure. Solids in liquid streams could plug or destroy equipment. Kuebler and McKinley worked with such solids as benzene and n-butane. They designed a single pass continuous flow apparatus; any solid was separated out from the following stream by a 5 micron sintered stainless steel filter; a gas chromatograph performed the assay. At LNG temperatures n-hexane is soluble in liquid methane to about 1000 ppm while for toluene the figure is about 100 ppm and benzene is 7 ppm. (Kuebler and McKinley, 1973). Measurements were made for the solubility of n-butane and n-pentane in liquid methane. These solubilities were much higher in the range of hundreds to thousands of ppm (Kuebler and McKinley, 1975).

Wilson, of Brigham Young University, also experimentally studied vapor-liquid equilibria at -127°C for the following binary mixtures, nitrogen-methane, nitrogen-ethane, methane-ethane, and methane-propane and correlated the data to prepare binary interaction coefficients. These were used to calculate bubble points for several LNG compositions at 0.68 Atm to 1.22 Atm. He fitted an equation to the data. Comparison with literature data showed reasonable agreement (Wilson, 1973).

Rodosevich and Miller developed a theoretical model relating the density of LNG to the components' concentration, in an effort partially funded by the AGA. Empirical

correlations often perform well only over the range of data used in establishing that correlation, but a theoretical model can have a broader range, if done properly. Here molecules in the liquid state of the LNG components were modeled as being almost but not quite hard spheres. They prepared a set of equations for calculating the excess volume for LNG mixtures. Data is naturally sparse in this region but they were able to demonstrate reasonable agreement between their predictions and the known values for both binary and ternary mixtures. Excess volume is extremely important in calculating mixture properties (Rodosevich and Miller, undated).

Barsuck and Surkov of the All-Union Scientific Research Institute of Natural Gas, Moscow, have developed a method for calculating the thermodynamic properties of natural gas. They began by modifying the Redlich-Kwong equation of state for vapor liquid equilibria. To calculate the enthalpy they used the same modification of the Redlich-Kwong equation to evaluate the isothermal pressure effect on the enthalpy of the mixtures in question. Experimental data were compared to calculated values from their modified equation and, they claimed, showed acceptable agreement. They said that comparison between their model and several others showed theirs to be the best (Barsuk and Surkov, 1974).

Agrewal and Laverman, of Chicago Bridge and Iron, a major builder of LNG tanks, measured the frost point temperature for the methane-carbon dioxide-nitrogen system. This frost point temperature determination is very important, because solids in liquid flow streams could plug lines and damage apparatus such as turbine blades. Carbon dioxide is usually present in natural gas in small concentrations and must be largely removed before liquefaction. Their experimental procedure was straightforward - the mixture was admitted to the test chamber and the appearance of the first solid was noted visually. A cold spot was maintained about 0.5°C to 1.0°C below the bulk temperature. The Bennedict-Webb-Rubin equation of state was used for comparing experimental data with a theoretical model. This comparison showed an average discrepancy for the 42 binary measurements of about 1.4°C. They extended their work to the ternary system methane-nitrogen-carbon dioxide by modeling the first two components as a pseudo single component. Agreement between the experimental values and this model was satisfactory (Agrawal and Laverman, 1973).

Custody transfer is a very important problem for the LNG industry, because errors can be extremely costly. Simonds Precision has had long experience with the capacitance-type of densitometer. Stuart discussed the work performed in developing and calibrating their

dielectric-type instrumentation. Initial densities were determined by direct measurement, weighing the container first empty and then full, and determining the volume by filling with water and weighing. To check on the accuracy of this method, the density of boiling liquefied nitrogen was measured to within 0.2%. The instrument was tested in the field at the Everett, Massachusetts facility of Distrigas, in an LNG tank truck fill line. The densitometer readings were compared to the densities calculated by Distrigas' own technique based on measured LNG compositions; 90% of the measured values were within 0.25% of the calculated and there appeared to be less scatter then in the Distrigas values. The calculation technique used by Simonds Precision for their baseline measurement was based on the work of Klosek and McKinley and of Boyl, which required the LNG composition and its density. The baseline technique gave consistently higher densities by an average of 0.5% than Distrigas' technique (Stuart, 1974).

Blanchard, of Foxboro/Transonics, Inc., discussed density measurements in custody transfer systems. He evaluated three techniques that are used by his company in measuring LNG density. The first, temperature measurement and composition, gave density through the use of a model such as that of Klosek and McKinley; Blanchard felt that the model did not give sufficient accuracy. The second, Archimedes force, was independent of any model. The third, dielectric constant and composition, was based on the principle that the dielectric constant can give very accurate molar densities over the temperature range around the boiling point of LNG, but the composition must be known because the relationship between density and dielectric constant is different for each component. Tests with Foxboro instruments and liquefied nitrogen showed errors of less than about 0.1% for the Archimedes and dielectric constant techniques (Blanchard, 1975).

Phannenstiel, of Air Products and Chemicals, Inc., experimentally determined the concentration of mercury in natural gas. Mercury had been reported as having damaged one train of a multitrain liquefaction unit, corroding aluminum heat exchangers. Measurements were made on ten different samples of natural gas, using an ultraviolet photometer; concentrations ranged from 0.0005 ppb to 13.1 ppb. The sensitivity of the technique was good, with a detection limit of 0.01 ppb, although values as low as 0.0005 ppb had been determined. Laboratory tests revealed two ways for mercury to corrode aluminum, both beginning with a weakening of the aluminum oxide surface layer, one by forming an aluminum-mercury amalgam and the other by forming aluminum hydroxide and gaseous hydrogen by the reaction of the amalgam with water in the presence of inorganic ions. Tests showed that mercury would not significantly corrode aluminum unless liquid water was present. Condensed water is not normally present in cryogenic heat exchangers, however (Phannenstiel et al, 1976).

The measurement of physical properties is very important to the LNG industry. The difficulties are great but the data is needed. The NBS work and that of others, being in the open literature, will not only add to the publically known data base, but might well provide the data for some fundamental insights into the area of cryogens and their mixtures near their boiling points. Those companies that have published data rather than keeping it for internal use are to be congratulated. They should be encouraged to continue making data public, and those companies not releasing data should be encouraged to publish as well.

D. Gelation

Almost all LNG safety research and development is focused on either how to prevent a release of LNG into the environment or how to mitigate the effects from an accidental release. It was thought that little could be done to alter the material itself. Recent work, however, has demonstrated that LNG can be converted into a thixotropic gel. In theory such a gel would reduce the liquid spread rate on both land and water after it leaves the tank; to the extent that the gel's yield strength exceeds the static pressure of the gel inside the ruptured tank the cargo might not leave the tank at all. Also, the gelation process should increase the stability of the vapor film between the gel and the warm substrait it contacts; that is, with gelation film boiling is favored over nucleate boiling, and so the vaporization rate per unit area is reduced significantly. In theory, then, LNG could be altered to present less of a risk in case of spill. To the extent that the vaporization rate is reduced in a spill, the vapor cloud will be smaller in size but of longer duration; a pool fire similarly will be smaller but of longer duration. Normal operations will benefit as well due to the material and financial savings with less boiloff. Since it is a thixotropic material, it may be possible to use existing pumps for loading and offloading without changes. How the gellant would be removed from the LNG, how existing equipment would have to be modified, and how cost-effective the process would be are important questions.

Shanes of the Massachusetts Institute of Technology prepared gelled liquefied methane using colloidal particles (1 to 1000 nm) of methanol and of water. Hydrocarbon mixtures were liquefied to simulate LNG. These gels reduce the vaporization rate by a factor of two or three by preventing the shift from film boiling to nucleate boiling. Generally, these gels are non-Newtonian fluids with time dependent rheological properties. At high shear rates, gels behave as Bingham plastics. Dynamic yield stresses, measured using an oscillating force, ranged from about 10 dynes/cm^2 to about 900 dynes/cm^2. Static yield stresses, measured by the height of the gel that can support itself, again ranged from 10 dynes/cm^2 to 900 dynes/cm^2. The greater the concentration of gelant, the greater the yield stress. Gelant concentrations varied up to about 6 weight percent. (Shanes, 1977). How long these gels remain effective was not discussed.

The Aerojet Energy Conversion Company has been involved in the gelation of cryogens since 1962. In a successful proposal to the U. S. Department of Energy (DOE) they described their experience and future plans. There is a degree of continuity between Shanes' work and

Aerojet's, since Shanes used Aerojet's method for gel formation. Aerojet has gelled methane with particles made with water, methanol, trimethylaminoborane, and trimethylaminoboron trifluoride, in concentrations as low as 1% by weight. The gelling agent should have the following attributes, they said: high volatility at ambient temperatures, no ash during combustion, thermal stability to avoid pyrolysis below 450°C, be non-corrosive, possess fuel value, and be inexpensive. They intend to experiment with water and methanol. To prepare the gel, a stream of gelant vapor diluted with a carrier gas is injected through a heated tube below the cryogen. The project for DOE will have five parts: gel preparation, gel characterization, safety tests, preliminary design of an industrial scale gelation system, and a preliminary economic assessment (Aerojet, 1977).

The Energy & Minerals Research Company has been involved in the gelation of liquids and liquefied gases. They have successfully gelled methane, propane, butane, nitrogen, hydrogen, and ammonia. They observed that the vaporization rate for gelled liquefied nitrogen is considerably reduced over that for nongelled liquefied nitrogen (Energy & Minerals Research Company, 1977).

Many questions remain about LNG gellation and it is too early to say whether it will be technically and economically feasible to use the process. If it is feasible to use, it would increase the overall level of safety of the LNG industry and conserve LNG through reduction of cargo vaporization.

V. CONCLUSION

Clearly the foregoing description of LNG safety research demonstrates the vast scope of the many programs. Future work should be limited to "fine tuning" the present understanding of LNG and to the evaluation of new technologies. The basic knowledge needed to safely design, operate, and regulate LNG storage and transportation systems is in hand. Now is the time to turn to other, newer hazardous chemicals, of which there are many less well understood than LNG.

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